



*JH*

# UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE  
United States Patent and Trademark Office  
Address: COMMISSIONER FOR PATENTS  
P.O. Box 1450  
Alexandria, Virginia 22313-1450  
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/730,166	12/05/2003	Jean Dominique Turgis	C-504 CIP	2931

7590 03/31/2006

Sun Chemical Corporation  
222 Bridge Plaza South  
Fort Lee, NJ 07024

EXAMINER
----------

SHOSHO, CALLIE E

ART UNIT	PAPER NUMBER
----------	--------------

1714

DATE MAILED: 03/31/2006

Please find below and/or attached an Office communication concerning this application or proceeding.

Best Available Copy

<b>Office Action Summary</b>	<b>Application No.</b>	<b>Applicant(s)</b>	
	10/730,166	TURGIS ET AL.	
	<b>Examiner</b>	<b>Art Unit</b>	
	Callie E. Shosho	1714	

**-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --**

**Period for Reply**

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
  - If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
  - Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133).
- Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

**Status**

- 1) ☐ Responsive to communication(s) filed on \_\_\_\_.
- 2a) ☐ This action is **FINAL**.                      2b) ☒ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

**Disposition of Claims**

- 4) ☒ Claim(s) 1-15 is/are pending in the application.
- 4a) Of the above claim(s) \_\_\_\_ is/are withdrawn from consideration.
- 5) ☐ Claim(s) \_\_\_\_ is/are allowed.
- 6) ☒ Claim(s) 1-15 is/are rejected.
- 7) ☐ Claim(s) \_\_\_\_ is/are objected to.
- 8) ☐ Claim(s) \_\_\_\_ are subject to restriction and/or election requirement.

**Application Papers**

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☒ The drawing(s) filed on 05 December 2003 is/are: a) ☒ accepted or b) ☐ objected to by the Examiner.
- Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
- Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

**Priority under 35 U.S.C. § 119**

- 12) ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☐ All    b) ☐ Some \* c) ☐ None of:
1. ☐ Certified copies of the priority documents have been received.
2. ☐ Certified copies of the priority documents have been received in Application No. \_\_\_\_.
3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).
- \* See the attached detailed Office action for a list of the certified copies not received.

**Attachment(s)**

- |  |   |
|--|---|
| 1) <input checked="" type="checkbox"/> Notice of References Cited (PTO-892)                        | 4) <input type="checkbox"/> Interview Summary (PTO-413)                     |
| 2) <input type="checkbox"/> Notice of Draftsperson's Patent Drawing Review (PTO-948)               | Paper No(s)/Mail Date. ____   |
| 3) <input checked="" type="checkbox"/> Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08) | 5) <input type="checkbox"/> Notice of Informal Patent Application (PTO-152) |
| Paper No(s)/Mail Date <u>2/19/04 &amp; 4/11/05</u>   | 6) <input type="checkbox"/> Other: ____                                     |

**DETAILED ACTION**

**Claim Rejections - 35 USC § 102**

1. The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

A person shall be entitled to a patent unless –

(e) the invention was described in (1) an application for patent, published under section 122(b), by another filed in the United States before the invention by the applicant for patent or (2) a patent granted on an application for patent by another filed in the United States before the invention by the applicant for patent, except that an international application filed under the treaty defined in section 351(a) shall have the effects for purposes of this subsection of an application filed in the United States only if the international application designated the United States and was published under Article 21(2) of such treaty in the English language.

2. Claims 6-8 and 14-15 are rejected under 35 U.S.C. 102(e) as being anticipated by  
Noguchi et al. (U.S. 6,790,875)

Noguchi et al. disclose aqueous energy curable ink comprising metallic colorant and energy curable vehicle made of homogenous, aqueous composition comprising 40-90% water, 1-30% ethylenically unsaturated resin containing neutralized functional groups, and photoinitiator. There is also disclosed method of printing comprising applying to a substrate the above ink and subjecting the substrate to actinic radiation to form an energy cured water resistant printed product (col.1, lines 10-18, col.3, line 65-col.4, line 9, col.4, lines 20-21, col.7, lines 5-15, col.21, lines 40-62, col.22, lines 4-18, col.25, lines 44-49, col.25, line 61-col.26, line 2, col.28, lines 21-48, col.29, lines 12-55, and col.30, lines 6-13).

In light of the above, it is clear that Noguchi et al. anticipate the present claims.

**Claim Rejections - 35 USC § 103**

3. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

The factual inquiries set forth in *Graham v. John Deere Co.*, 383 U.S. 1, 148 USPQ 459 (1966), that are applied for establishing a background for determining obviousness under 35 U.S.C. 103(a) are summarized as follows:

1. Determining the scope and contents of the prior art.
2. Ascertaining the differences between the prior art and the claims at issue.
3. Resolving the level of ordinary skill in the pertinent art.
4. Considering objective evidence present in the application indicating obviousness or nonobviousness.

4. This application currently names joint inventors. In considering patentability of the claims under 35 U.S.C. 103(a), the examiner presumes that the subject matter of the various claims was commonly owned at the time any inventions covered therein were made absent any evidence to the contrary. Applicant is advised of the obligation under 37 CFR 1.56 to point out the inventor and invention dates of each claim that was not commonly owned at the time a later invention was made in order for the examiner to consider the applicability of 35 U.S.C. 103(c) and potential 35 U.S.C. 102(e), (f) or (g) prior art under 35 U.S.C. 103(a).

5. Claims 1-15 are rejected under 35 U.S.C. 103(a) as being unpatentable over Laksin et al. (U.S. 2003/0154871) in view of Tanaka et al. (U.S. 5,587,405).

Laksin et al. disclose aqueous, energy curable printing ink comprising pigment wherein the ink is formulated using a single phase, i.e. homogenous, composition comprising 5-50% water, ethylenically unsaturated resin containing neutralized acidic or basic functional groups, water-insoluble oligomer, water-soluble oligomer, and photoinitiator. There is also disclosed method of printing comprising applying the ink to substrate and then subjecting the substrate to actinic radiation. Although there is no disclosure that the ink is water resistant, given that Laksin et al. disclose ink identical to that presently claimed, it is clear that the ink is inherently water resistant (paragraphs 20-33, 35, 39, 62, 71-80, 92-102, 103-109, and claim 3). Attention is drawn to example of paragraphs 103-109 that discloses ink comprising 30.5% water and 9% neutralized resin.

The difference between Laksin et al. and et al. and the present claimed invention is the requirement in the claims of specific pigment.

Laksin et al. disclose the use of pigment, however, there is no disclosure of the use of metallic pigment as presently claimed.

Tanaka et al., which is drawn to radiation curable ink, disclose the use of metal pigment such as metal powder in order to produce ink with fast color having strong light resistance. Tanaka et al. also disclose the equivalence and interchangeability of using organic pigment or carbon black, as disclosed by Laksin et al., with using the metal pigment (col.14, line 62-col.15, line 21).

In light of the above, it therefore would have been obvious to one of ordinary skill in the art to use metal pigment in the ink of Laksin et al. in order to produce ink with fast color having strong light resistance, and thereby arrive at the claimed invention.

6. Claims 6-8 and 14-15 are rejected under 35 U.S.C. 103(a) as being unpatentable over Gummeson (U.S. 2002/0198289) in view of Tanaka et al. (U.S. 5,587,405).

Gummeson discloses aqueous, energy curable, homogenous ink comprising at least 50% aqueous carrier medium comprising 30-100% water and 0-70% solvent, pigment, 20-50% UV curable resin having neutralized functional groups, and photoinitiator. There is also disclosed method of printing comprising applying to a substrate the above ink and subjecting the substrate to actinic radiation to form an energy cured water resistant printed product (paragraphs 2, 19-22, 26-27, 34, 40-42, 48, 59, and 75-77).

The difference between Gummeson and et al. and the present claimed invention is the requirement in the claims of specific pigment.

Gummeson discloses the use of pigment, however, there is no disclosure of the use of metallic pigment as presently claimed.

Tanaka et al., which is drawn to radiation curable ink, disclose the use of metal pigment such as metal powder in order to produce ink with fast color having strong light resistance.

Tanaka et al. also disclose the equivalence and interchangeability of using organic pigment or carbon black, as disclosed by Gummeson, with using the metal pigment (col.14, line 62-col.15, line 21).

In light of the above, it therefore would have been obvious to one of ordinary skill in the art to use metal pigment in the ink of Gummeson in order to produce ink with fast color having strong light resistance, and thereby arrive at the claimed invention.

7. Claims 1-15 are rejected under 35 U.S.C. 103(a) as being unpatentable over WO 99/19369 in view of Thanawalla et al. (U.S. 4,745,138) and Tanaka et al. (U.S. 5,587,405).

WO 99/19369 discloses aqueous energy curable printing ink comprising pigment and aqueous solution, i.e. homogenous, of water, diluent, 5-25% ethylenically unsaturated resin having neutralized functional groups, and photoinitiator. There is also disclosed method of printing comprising applying to a substrate the above ink and subjecting the substrate to actinic radiation to form an energy cured water resistant printed product. Attention is drawn to example 9 that discloses ink comprising 46% water, 20% neutralized resin, water-soluble oligomer, pigment, and photoinitiator. Although there is no disclosure that the ink is water resistant, given that WO 99/19369 discloses ink identical to that presently claimed, it is clear that the ink is inherently water resistant (page 1, 1<sup>st</sup> paragraph, page 3, 3<sup>rd</sup> full paragraph, page 4, 1<sup>st</sup> paragraph, paragraph bridging pages 4-5, paragraph bridging pages 5-6, page 6, 2<sup>nd</sup> full paragraph – page 7, last paragraph, paragraph bridging pages 8-9, paragraph bridging pages 9-10, page 10, 1<sup>st</sup> full paragraph, example 9, and example 12). For specific details regarding the diluent, WO 99/19369 refers to Thanawalla et al. which discloses the use of diluent that is one or more, i.e. combination, water-soluble oligomer and water-insoluble oligomer (col.5, line 62-col.6, line 15 and col.6, lines 44-60).

The difference between WO 99/19369 and the present claimed invention is the requirement in the claims of specific pigment.

WO 99/19369 discloses the use of pigment, however, there is no disclosure of the use of metallic pigment as presently claimed.

Tanaka et al., which is drawn to radiation curable ink, disclose the use of metal pigment such as metal powder in order to produce ink with fast color having strong light resistance. Tanaka et al. also disclose the equivalence and interchangeability of using organic pigment, as disclosed by WO 99/19369, with using the metal pigment (col.14, line 62-col.15, line 21).

In light of the above, it therefore would have been obvious to one of ordinary skill in the art to use metal pigment in the ink of WO 99/19369 in order to produce ink with fast color having strong light resistance, and thereby arrive at the claimed invention.

8. Claims 1-2, 6-7, 9, and 14 are rejected under 35 U.S.C. 103(a) as being unpatentable over Phillips et al. (*Radiation Curable Water Dilutable Polyester Acrylates*).

Phillips et al. disclose aqueous energy curable printing ink comprising pigment, photoinitiator, and aqueous solution, i.e. homogenous, of water, water-soluble ethylenically unsaturated oligomer, i.e. polyethylene glycol diacrylate, and ethylenically unsaturated resin having neutralized functional groups. There is also disclosed method of printing comprising applying to a substrate the above ink and subjecting the substrate to actinic radiation to form an energy cured water resistant printed product (pages 1-2).

The difference between Phillips et al. and the present claimed invention is the requirement in the claims of specific pigment.

Phillips et al. disclose the use of pigment, however, there is no disclosure of the use of metallic pigment as presently claimed.



Art Unit: 1714

Tanaka et al., which is drawn to radiation curable ink, disclose the use of metal pigment such as metal powder in order to produce ink with fast color having strong light resistance (col.14, line 62-col.15, line 21).

In light of the above, it therefore would have been obvious to one of ordinary skill in the art to use metal pigment in the ink of Phillips et al. in order to produce ink with fast color having strong light resistance, and thereby arrive at the claimed invention.

9. Claims 1-5, 9, and 11-13 are rejected under 35 U.S.C. 103(a) as being unpatentable over Noguchi et al. (U.S. 6,790,875) in view of Figov (U.S. 5,623,001).

Noguchi et al. disclose aqueous energy curable ink comprising metallic colorant and energy curable vehicle made of homogenous, aqueous composition comprising 40-90% water, 1-30% ethylenically unsaturated resin containing neutralized functional groups, and photoinitiator. There is also disclosed method of printing comprising applying to a substrate the above ink and subjecting the substrate to actinic radiation to form an energy cured water resistant printed product (col.1, lines 10-18, col.3, line 65-col.4, line 9, col.4, lines 20-21, col.7, lines 5-15, col.21, lines 40-62, col.22, lines 4-18, col.25, lines 44-49, col.25, line 61-col.26, line 2, col.28, lines 21-48, col.29, lines 12-55, and col.30, lines 6-13).

The difference between Noguchi et al. and the present claimed invention is the requirement in the claim of ethylenically unsaturated oligomer.

Figov, which is drawn to aqueous energy curable ink, discloses the use of ethylenically unsaturated oligomer in order to produce ink with sufficient film-forming properties to effectively dry during curing (col.3, line 45-col.4, line 4).

In light of the motivation for using ethylenically unsaturated oligomer disclosed by Figov as described above, it therefore would have been obvious to one of ordinary skill in the art to use ethylenically unsaturated oligomer in the ink of Noguchi et al. in order to produce ink with sufficient film-forming properties so that the ink effectively dries during curing, and thereby arrive at the claimed invention.

10. The prior art made of record and not relied upon is considered pertinent to applicant's disclosure.

EP 287019 discloses radiation curable composition comprising neutralized resin, ethylenically unsaturated oligomer, and photoinitiator, however, there is no disclosure that the composition comprises water or metallic pigment as required in all the present claims. While the composition is developable by an aqueous developer, there is no disclosure that the composition itself comprises water.

Laksin et al. (U.S. 6,232,361) and Samaranayake (U.S. 6,743,514) each disclose aqueous energy curable ink comprising water, pigment, cationic polymerizable compound, cationic initiator, resin, and ethylenically unsaturated oligomer, however, there is no disclosure that the resin has neutralized functional groups or any disclosure of metallic pigment as required in all the present claims.

EP 35574 discloses protective coating comprising water and neutralized resin, however, there is no disclosure that the composition comprises metallic pigment as required in all the present claims or any disclosure of ethylenically unsaturated oligomer as required in present claim 1 and 9. EP 35574 also discloses radiation curable ink comprising ethylenically

Art Unit: 1714

unsaturated oligomer, resin having neutralized groups, metallic colorant, and photoinitiator, however, there is no disclosure that the ink comprises water as required in all the present claims.

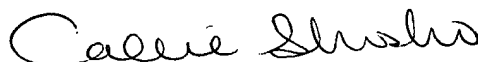
Beck et al. (U.S. 2003/0152715) discloses aqueous, radiation curable ink comprising water, ethylenically unsaturated oligomer, pigment, and resin, however, there is no disclosure that the resin has neutralized functional groups or any disclosure of metallic pigment or homogeneous vehicle as required in all the present claims.

11. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Callie E. Shosho whose telephone number is 571-272-1123. The examiner can normally be reached on Monday-Friday (6:30-4:00) Alternate Fridays Off.

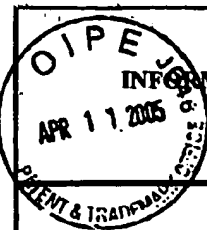
If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Vasu Jagannathan can be reached on 571-272-1119. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

CS  
3/24/06

  
Callie E. Shosho  
Primary Examiner  
Art Unit 1714





## INFORMATION DISCLOSURE CITATION

(Use several sheets if necessary)

Docket Number (Optional)

C-504 CIP

Application Number

10/730,166

Applicant(s)

Turgis et al.

Filing Date

December 5, 2003

Group Art Unit

1755-1714

## U.S. PATENT DOCUMENTS

*EXAMINER INITIAL	REF	DOCUMENT NUMBER	DATE	NAME	CLASS	SUBCLASS	FILING DATE IF APPROPRIATE
CS		4,264,483	04/28/81	Laufer et al.	260	23	
CS		4,113,895	09/12/78	Watt et al.	427	44	

## U.S. PATENT APPLICATION PUBLICATIONS

*EXAMINER INITIAL	REF	DOCUMENT NUMBER	DATE	NAME	CLASS	SUBCLASS	FILING DATE IF APPROPRIATE
CS		2003/0152715	08/14/03	Beck et al.	427	496	

## FOREIGN PATENT DOCUMENTS

	REF	DOCUMENT NUMBER	DATE	COUNTRY	CLASS	SUBCLASS	Translation	
							YES	NO
CS		03/093378	11/13/03	WO				
CS		00/40630	07/13/00	WO				

## OTHER DOCUMENTS

(Including Author, Title, Date, Pertinent Pages, Etc.)


EXAMINER

Celene Shusho

DATE CONSIDERED

3/22/06

EXAMINER: Initial if citation considered, whether or not citation is in conformance with MPEP Section 609; Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

<b>Notice of References Cited</b>	Application/Control No. 10/730,166		Applicant(s)/Patent Under Reexamination TURGIS ET AL.	
	Examiner Callie E. Shosho		Art Unit 1714	Page 1 of 1

**U.S. PATENT DOCUMENTS**

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	Classification
*	A	US-6,790,875 B2	09-2004	Noguchi et al.	522/84
*	B	US-2003/0154871 A1	08-2003	Laksin et al.	101/211
*	C	US-5,587,405 A	12-1996	Tanaka et al.	522/98
*	D	US-2002/0198289 A1	12-2002	Gummeson	523/400
*	E	US-5,623,001 A	04-1997	Figov	522/84
*	F	US-6,232,361 B1	05-2001	Laksin et al.	522/84
*	G	US-6,743,514 B1	06-2004	Samaranayake	428/441
	H	US-			
	I	US-			
	J	US-			
	K	US-			
	L	US-			
	M	US-			

**FOREIGN PATENT DOCUMENTS**

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	Classification
	N	WO 99/19369 A2	04-1999	_____	ROONEY et al.	_____
	O	EP 035574 A1	08-1980	_____	ARAI et al.	_____
	P					
	Q					
	R					
	S					
	T					

**NON-PATENT DOCUMENTS**

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	
	V	
	W	
	X	

\*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)  
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C08F</b>	<b>A2</b>	<b>(11) International Publication Number:</b> <b>WO 99/19369</b> <b>(43) International Publication Date:</b> 22 April 1999 (22.04.99)
<b>(21) International Application Number:</b> PCT/US98/22035 <b>(22) International Filing Date:</b> 16 October 1998 (16.10.98)  <b>(30) Priority Data:</b> 60/062,185      16 October 1997 (16.10.97)      US  <b>(71) Applicant (for all designated States except US):</b> SUN CHEMICAL CORPORATION [US/US]; 222 Bridge Plaza South, Fort Lee, NJ 07024 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> ROONEY, John [US/US]; 32 Berkeley Circle, Basking Ridge, NJ 07020 (US). CHATTERJEE, Subhankar [US/US]; 60 Norma Road, Hampton, NJ 08827 (US). LAKSIN, Mikhail [US/US]; 2278 Redwood Road, Scotch Plains, NJ 07076 (US). TURGIS, Jean-Dominique [FR/FR]; 214 Feronia Way, Rutherford, NJ 07070 (US).  <b>(74) Agent:</b> PERSLEY, Sidney; 222 Bridge Plaza South, Fort Lee, NJ 07024 (US).		<b>(81) Designated States:</b> CA, JP, MX, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>
<b>(54) Title:</b> PHOTONEUTRALIZATION OF pH SENSITIVE AQUEOUS POLYMERIC DISPERSIONS AND METHODS FOR USING SAME  <b>(57) Abstract</b>  An aqueous polymer dispersion comprising a polymer substantially free of cationic polymerizable groups and a cationic photoinitiator, wherein the polymer is capable of being precipitated by an acid or base generating photoinitiator upon exposure to radiation and is optionally an energy curable polymer.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						



PHOTONEUTRALIZATION OF pH SENSITIVE AQUEOUS POLYMERIC  
DISPERSIONS AND METHODS FOR USING SAME

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to photoneutralized, pH sensitive, aqueous polymeric dispersions.

Description of Related Art

Free radical polymerizable compositions offer a number of advantages over heat or ambient temperature curing, including: rapid curing at ambient temperatures; elimination of solvents and the environmental problems associated with their use; elimination of solvent recovery; elimination of the use of fossil fuels for curing and their polluting effects; and the capability of coating heat sensitive substrates. However, radiation curing at times introduces its own difficulties, such as in connection with formulating compositions having varying degrees of viscosity; use of toxic components and inhibition of curing by air contact. These difficulties may be substantially overcome by selective formulation of the radiation curable composition, and hence, the selection of the components of the radiation curable composition becomes critical.

Radiation curable compositions are well known in the art. Monomers typically used for such purpose include acrylic and methacrylic acid esters of various diols and triols, such as 1,6-hexanediol, diethylene glycol, 1,4-butanediol, trimethoxypropane, pentaerythritol or glycerol, along with alkoxyated monomers, such as ethoxyated and propoxyated derivatives thereof. Typical examples of radiation curable compositions

employing some of the above-described monomers have been described in U.S. Patents 3,594,410 and 3,380,831, which are concerned with printing and thermal transfer reproductive elements. U.S. Patents 3,912,670; 4,025,548; 4,183,796; 4,243,500; 4,360,540; and 4,404,075 teach radiation curable coating and adhesive compositions. It is also well known to prepare radiation curable compositions using specialized polymerizable materials. For example, U.S. Patents 4,994,346; 5,308,744; 5,300,380; 5,585,222; and 5,498,765 teach film forming photoreactive polymeric compositions for use in photoresist materials. The polymeric material employed in each case, however, contains cationic polymerizable groups. U.S. Patents 5,206,116; 5,296,332; and 5,384,229 describe film forming photoreactive polymers that also contain cationic polymerizable systems for use in electrodeposition or solder masking. In U.S. Patents 3,356,461 and 3,342,787, esters of styrene maleic anhydride copolymers are used. U.S. Patents 3,862,067 and 3,884,856 disclose styrene maleic anhydride copolymers derived from low molecular weight copolymers of styrene and maleic anhydride. U.S. Patents 3,825,430 and 4,401,793 teach the use of polymerizable esters prepared by reacting an anhydride-containing polymer with an excess of hydroxyalkylacrylate or methacrylate wherein the esters are free of unreacted anhydride groups. French Patent 2,253,772 describes the use of styrene-maleic anhydride polymers having free hydroxyl groups. U.S. Patent 4,293,636 teaches a photopolymerizable composition containing polyester, half esterified hydroxyalkylacrylate of polybasic acid and vinyl monomer. However, all of these references teach radiation curable compositions containing organic solvents.

Representing a departure from solvent based

radiation curable compositions, European Patent 0 257 554 A2 teaches a radiation curable composition employing a stable aqueous dispersion of polymers produced from a monomer containing ethylenic unsaturation and pendant cationic ethylenic functionalities. The polymers cross-link upon exposure to radiation in the presence of a cationic photoinitiator. U.S. Patent 4,745,138 describes a radiation curable composition comprising low molecular weight partial ester of free anhydride-containing copolymers. These polymers, however, are not water soluble or dispersible due to the free anhydride functionalities.

For the most part, the prior art does not teach aqueous polymer dispersions or solutions wherein in the presence of a cationic photoinitiator, the polymer precipitates out of the dispersion or solution to form a film upon exposure to radiation.

The prior art does not teach aqueous polymer dispersions or solutions wherein in the presence of a cationic photoinitiator, the polymer precipitates out of the dispersion or solution to form and undergo cross-linking upon exposure to radiation.

It is a primary object of the present invention to provide an aqueous polymer dispersion or solution wherein in the presence of a cationic photoinitiator, the polymer does not polymerize but precipitates out of solution to form a film.

It is also an object of the present invention to provide an aqueous polymer dispersion or solution wherein in the presence of a cationic photoinitiator, the polymer does not polymerize but precipitates out of solution to form a free radical cross-linkable film when exposed to radiation.

Another object of the present invention is to

prepare simple and inexpensive printing inks and coatings using these aqueous polymer dispersions.

Another object of the present invention is to prepare simple and inexpensive energy curable printing inks and coatings using these aqueous polymer dispersions.

These and other objects, which will become apparent from the following description of the present invention.

#### SUMMARY OF THE INVENTION

In one aspect the invention is an energy curable basic aqueous polymer dispersion wherein the polymer is substantially free of cationic polymerizable functionalities and capable of being precipitated from the dispersion in the presence of an acid generating photoinitiator upon exposure to radiation.

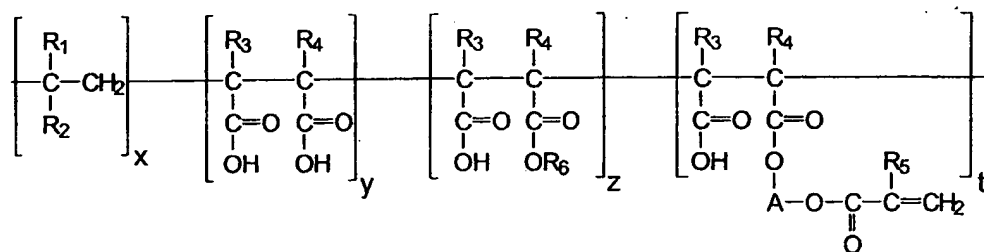
In another aspect the invention is a water based energy curable coating and ink composition employing these energy curable basic aqueous polymer dispersions.

#### DETAILED DESCRIPTION OF THE INVENTION

The invention extends the use of radiation curing technology to the vast and economical array of water based polymer systems used in water base printing and coating. Water base polymeric systems typically contain acidic or basic functional resins neutralized to a certain pH by a base or acid, respectively, in order to solubilize the resin or resin system in water. As in the prior art, the polymers of the present invention are neutralized and are soluble or dispersible in aqueous medium. However, unlike prior art polymers, the polymers of the present invention are substantially free of cationic polymerizable functionalities and thereby avoid cross-linking via a cationic mechanism when exposed to

radiation. The polymer, may however, optionally contain free radical polymerizable functionalities rendering it capable of cross-linking via a free radical mechanism upon exposure to radiation.

Three essential characteristic features are required of the polymers suitable for use in the present invention: a) the polymer must be substantially free of cationic polymerizable functionalities; b) the polymer must be soluble or dispersible in a basic aqueous solution and an acid generating photoinitiator; and (c) the polymer must precipitate out of such solution upon exposure to radiation. Polymers suitable for use in the present invention, for example, may include polyamide resins, acrylic resins, acrylated acrylic resins, amino resins, polyester resins, urethane resins, starch, polysulfonate resins, phenolic resins and melamine resins. In addition to meeting these requirements the polymer may optionally containing free radical polymerizable functionalities, for example, the class of compounds meeting these requirements would include copolymers of the general structure:



wherein:  $R_1$  and  $R_2$  are independently selected from the group consisting of hydrogen,  $C_1$ - $C_{20}$  alkyl,  $C_6$ - $C_{10}$  aryl,  $C_7$ - $C_{14}$  alkaryl,  $C_4$ - $C_{12}$  cycloalkyl and halogen such as chlorine, fluorine and bromine; and preferably are independently selected from hydrogen, methyl, phenyl, benzyl, or  $C_4$ - $C_6$  cycloalkyl;  $R_3$ ,  $R_4$  and  $R_5$  are

independently selected from the group consisting of hydrogen and  $C_1-C_5$  alkyl; and preferably are independently selected from hydrogen and/or methyl;  $R_6$  is selected from the group consisting of alkyl, aralkyl, alkyl substituted aralkyl and oxyalkylated derivatives of same containing 2 to 4 carbon atoms in each oxyalkylene group, which group may be 1 to 20 and preferably 1 to 6 repeating units; A is a linear or branched divalent  $C_1-C_{20}$  alkylene or oxyalkylated derivative thereof as described in connection with  $R_6$ ; and subscripts x, y, z and t are whole numbers such that the sum of x, y, z and t ranges from 3 to 20, with each being equal to or greater than 1.

In general, the polymerizable compositions of the present invention may be liquids or free flowing solids, depending upon their molecular weight, and are characterized by having a number average molecular weight if between about 1,000 and 20,000, preferably between 2,000 and 4,000, an acid number between 100 to 300 and preferably between 180 and 300, an acrylate equivalent per gram value of at least 0.1, preferably between 10 to 50 molar percent, and a glass transition temperature of at least about 40 degrees C and preferably between 50 and 100 degrees C.

The polymers containing free radical polymerizable functionalities, optionally employed in the present invention, may be prepared, for example, by reacting a styrene/maleic anhydride copolymer, a hydroxyl terminated acrylate and a monofunctional alcohol to form a partial ester. Next, any remaining anhydride functionalities would be opened with a water/ammonia mixture. The solvent would then removed through a solvent exchange process.

A reaction scheme for preparing the free radical polymerizable functionalities employed herein, for

example, may constitute adding methyl isobutyl ketone (MIBK) under agitation to a styrene maleic anhydride copolymer having an acid number of 480 and an average molecular weight of 1600. The two materials are then heated to approximately 95-110 degrees C over 1 to 2 hours under a nitrogen blanket. Next, N,N-dimethylbenzyl amine and a monofunctional alcohol such as n-propanol, ethanol or octadecanol are then added to form a polymeric mixture having an acid number between 200 to 210. The nitrogen blanket is then removed and 4-methoxyphenol and N,N-dimethylbenzylamine is added. Over a period of time, for example 60 to 90 minutes, a hydroxy-functional acrylate such as 4-hydroxybutyl acrylate or 2-hydroxyethyl acrylate is added until the acid number of the polymeric mixture is between 130 to 140. The polymeric mixture is then distilled and 4-methoxyphenol is added along with ammonium hydroxide and deionized water. The mixture is then heated, for example to 99 degrees C. The MIBK and water are then removed by distillation. When all of the MIBK has been removed, the water is returned to the mixture as a water/ammonia distillate.

The photoinitiators employed in the present invention, are selected from commercially available acid and base generating photoinitiators. While not wishing to be bound by theory, it is believed that the acidic or basic dispersion, which is photogenerated in the aqueous medium by the action of the radiation and photoinitiator, serves to instantly shift the equilibrium of the polymeric dispersion in the medium and cause the polymer to precipitate out of solution forming a film. Thus, where base generating photoinitiators are employed, acidic polymeric dispersions are preferred. Likewise, where acid generating photoinitiators are employed, basic polymeric dispersions are preferred.

Base generating photoinitiators suitable for use in the present invention include carbamates such as 3',5'-dimethoxybenzoin carbamate, orthonitrobenzyl carbamate; oximes such as orthophenylacetyl acetophenone oxime and 0,0'-succinyl diacetophenone oxime; and inorganic amines such as bromo (pentamine)cobalt(II) chloride, alkylamine cobalt; and complexes of the general structure  $\text{Co}(\text{NH}_2\text{Z}_5)(\text{K})_n$  where Z is a methyl or n-propyl group, K is chloride, bromide or perchlorate ion and n is an integer from 1 to 2.

Acid generating photoinitiators suitable for use in the present invention include diazonium salts; sulfonium salts; iodonium salts; ferrocinium salts; tetraphenylphosphonium tetrafluoro phosphate; phenanthrolium bis-hexafluorophosphate; diphenylsulfoxonium hexafluorophosphate; triphenylselenonium salts; triphenyltelluronium salts; 2,6-diphenyl-4-p-chloro phenylthiopyryliumtetrafluoroborate; and cyclopentadienyl isopropylbenzene Iron (II).

The preferred diazonium salts are selected from 2,5-diethoxy-4-(p-tolylmercapto)benzene diazonium hexafluorophosphate, 2,4,6-trichlorobenzene diazonium hexafluorophosphate, 2,4,6-tribromobenzene diazonium hexafluorophosphate, p-chloro benzene diazonium hexafluorophosphate.

The preferred sulfonium salts are selected from triarylsulfoniumhexafluorophosphate and triarylsulfonium hexafluoroantimonate.

The preferred iodonium salts are selected from diphenyliodoniumhexafluorophosphate, diphenyliodonium hexafluoroarsenate, diphenyliodoniumtrifluoromethane sulfonate, diaryliodoniumtrifluoromethane sulfonate and UV 9310-C (available from GE Silicones, Waterford, NY).

In addition to the optionally radiation curable,



photoneutralizable polymer and photoinitiator, small amounts of free radical photoinitiator and water soluble or dispersible diluents may be added to the aqueous dispersions of the invention for improved film performance properties. These water soluble or dispersible diluents include, but are not limited to, vinyl monomers such as lower alkyl esters of acrylic or methacrylic acid including methyl methacrylate, ethyl acrylate, 2-ethylhexyl acrylate, butyl acrylate and isobutyl methacrylate; vinyl esters such as vinyl acetate and vinyl propionate; vinyl halides; and high solvency monomers such as 2,2-ethoxyethoxyethyl acrylate, tetrahydrofurfuryl acrylate, n-laurylacrylate, 2-phenoxy ethyl acrylate, glycidyl acrylate, glycidylmethacrylate, isodecylacrylate, isooctyl acrylate. Other diluents include vinyl aromatics such as styrene, alphas-methyl styrene, vinyl toluene, indene and p-tert butyl styrene, fumaric acid, maleic anhydride and nitrogen containing monomers such as acrylonitrile, acrylamide, methacrylamide, N,N-dimethylacrylamide, N-vinylpyrrolidine and N-vinyl caprolactam. These and other suitable diluents are widely known and some are described in U.S. Patent 4,745,138 which is incorporated herein by reference. Generally the diluents and other additives must not be reactive with the photoneutralization of the polymer dispersion, i.e. will not copolymerize therewith, and shall be water soluble or dispersible. It is important that the additives and diluents do not interfere with the polymerization, photoneutralization or precipitation of the polymeric dispersion.

The amount of polymer having substantially free of cationic polymerizable functionalities employed in the energy curable compositions herein ranges from about 5 wt.% to about 25 wt.%; the amount of polymer having free

radical polymerizable functionalities used ranges from about 5 wt.% to about 50 wt.%; the amount of cationic photoinitiator used will typically range from about .01 wt.% to about 5 wt.%; and the amount of free radical photoinitiator used will typically range from about 2 wt.% to about 10 wt.%.

The curable compositions of the present invention are cured by means of radiation. As used herein, the term "radiation" shall mean electron beam, ultra-violet light, gamma rays, etc., but preferably the term means ultra-violet light or electron beam.

The aqueous polymeric dispersions of the present invention dry instantly. Thus, there is no need for water removal at or during curing. When used as a coating or printing ink, they may be applied by any suitable means, such as by spraying, dipping, flow coating, brushing and the like, followed by or simultaneously with irradiation. Since the energy curable compositions of the invention are aqueous based no volatile organic compounds (VOCs) are present which renders the compositions water washable. Also, the problem of transdermal migration of acrylates, common in many solvent based energy curable cross-linked systems, is also eliminated in these aqueous based dispersions.

The following examples will serve to illustrate the specific aspects of the present invention. The examples as well as other embodiments set forth in the specification are intended to be illustrative of the invention and shall not necessarily limit the scope thereof in any respect or be construed as such. In the examples and throughout the specification and claims, all parts and percentages are by weight unless otherwise expressly stated.

#### Example 1 (Comparative)

A water based blue printing ink was prepared by combining Sunspere BHD-6000 aqueous dispersion (40wt.%, pH 8, a Sunspere is trademark of the Sun Chemical Corporation, Fort Lee, NJ) and an acrylic aqueous dispersion (60 wt.%, E-1691 having a pH 5.7, available from Rohm and Hass Corporation, Philadelphia, PA). The resulting printing ink had a pH of 7.6.

#### Example 2

To the printing ink prepared in Example 1 was added Cyracure 6990 (5 parts, 50 vol% triarylsulfonium hexafluoro phosphate salt in propylene carbonate, Cyracure is a trademark of the Union Carbide Corporation, Danbury, CT).

#### Example 3

The printing inks of Examples 1 and 2 were each printed onto a polyester substrate with a flexographic printer and exposed to ultra-violet light (400 watt/inch @400 feet per minute). The printing ink of Example 1 was very soft, easily smeared surface and took at least 24 hours to dry. However, the printing ink of Example 2 dried immediately and had a non-smear surface, an indication of an ink having excellent substrate adhesion.

#### Example 4

A coating was prepared by removing the pigment from the formulation described in Example 2.

#### Example 5

The pH of the printing ink prepared in Example 2 was adjusted to a pH of 10 by adding ammonia. The printing

ink was then printed onto a polyester substrate and exposed to ultraviolet light (400 watt/inch @400 feet per minute). The printing ink dried immediately and had a non-smear surface.

#### Example 6 (Comparative)

A standard water based black printing ink was prepared with an epoxy ester based aqueous ink. The pH of the resulting ink was 8.5.

#### Example 7

To the ink prepared in Example 6 was added Cyracure 6990 photoinitiator (5 parts, 50 vol% triarylsulfonium-hexafluorophosphate salt in propylene carbonate). The pH of the resulting ink was 8.4.

#### Example 8

The printing inks of Examples 6 and 7 were each printed onto a polyester substrate with a flexographic printer and exposed to ultra-violet light (400 watt/inch @400 feet per minute). The printing ink of Example 6 was very soft surface and was easily smeared. However, the printing ink of Example 7 had a much harder, non-smear, surface.

#### Example 9

A black printing ink was prepared by adding a black pigment (15 wt.%), a water soluble epoxy polyacrylate (15 wt.%) (BASF Laromer 8765, available from BASF Corp., Mt. Olive, NJ), a reactive styrene maleic acrylated resin modified with hydroxyethyl acrylate (20 wt.%), water (46 wt.%), a free radical photoinitiator (2 wt.%, Irgacure 2959, Irgacure is a trademark of Ciba Specialties, Corp., Tarrytown, NY), a cationic photo initiator (1 wt.%, 50

vol% triarylsulfoniumhexafluorophosphate salt in propylene carbonate, Cyracure 6990), a wetting additive Tego Glide 435 (0.5 wt.%, Tego Glide is a trademark of Tego Chemie Service GmbH, Essen, Germany) and ammonia (0.5 wt.%). The resulting printing ink had a pH between 7 and 8.

The printing ink was applied to a metallized paper substrate with a flexographic printing device and exposed to ultraviolet light ( $240 \text{ mJ/cm}^2$  @200 feet per minute). The printing ink was resistant to 30 alcohol (e.g. methylethylketone) rubs and had a color density of 1.9.

#### Example 10

A red printing ink was prepared by adding Sunspense pigment dispersion (35 wt.%, of which 30 wt.% is pigment), Laromer 8765 (17 wt.%), reactive styrene maleic acrylated resin modified with hydroxyethyl acrylate (17 wt.%), water (27 wt.%), Irgacure 2959 (2 wt.%) and Cyracure 6990 (1 wt.%), Tego Glide 435 (0.5 wt.%) and ammonia (0.5 wt.%). The resulting printing ink had a pH between 7 and 8.

The printing ink was applied to a metallized paper substrate with a 450 line flexoanilox device and exposed to ultra-violet light ( $250 \text{ mJ/cm}^2$  @120 feet per minute). The printing ink was resistant to 50 alcohol rubs and had a color density of 2.0.

#### Example 11

A coating was prepared by adding an styrene maleic anhydride acrylate (20 wt.%), epoxy acrylate (30 wt.%, Laromer 8765) water (47 wt.%), and a iodonium hexafluoro-animonate photoinitiator (0.5 wt.%, UV9365C-D1, available from GE Silicones, Waterford, NY)

Example 12

An ink was prepared by adding a carbon black pigment to the procedure described in Example 11.

Example 13 (Comparative)

A coating was prepared by the procedure described in Example 11, except the iodonium hexafluoroanionate photoinitiator was omitted.

Example 14

The coatings of Examples 11 and 13 were applied to with a #2 rod and exposed to an electron beam (165kV, 2.6 Mrad, oxygen content less than 200 ppm, @50 feet per minute). The coating of Example 11 was resistant to between 70-90 alcohol rubs, whereas the coating of Example 13 was resistant to between 40-50 alcohol rubs.

Example 15

A coating was prepared by adding an styrene maleic anhydride acrylate modified with hydroxy ethyl acrylate (36 wt.%), an epoxy acrylate (10 wt.%, Laromer 8765, water (48 wt.%), Igracure 2959 (1 wt.%) and a cationic photoinitiator (1.0 wt.% Cyracure 6990).

The coating was odorless when applied with a #3 Mayer bar onto a leneta substrate. The coating was then exposed to ultra-violet light (400 watt/in @200 feet per minute). The rub resistance of the coating to alcohol (e.g. methyl ethyl ketone) was greater than 100 and the gloss was between 87 and 94. The scratch resistance was also excellent.

The present invention has been described in detail, including the preferred embodiments thereof. However, it will be apparent to those of skill in the art, upon

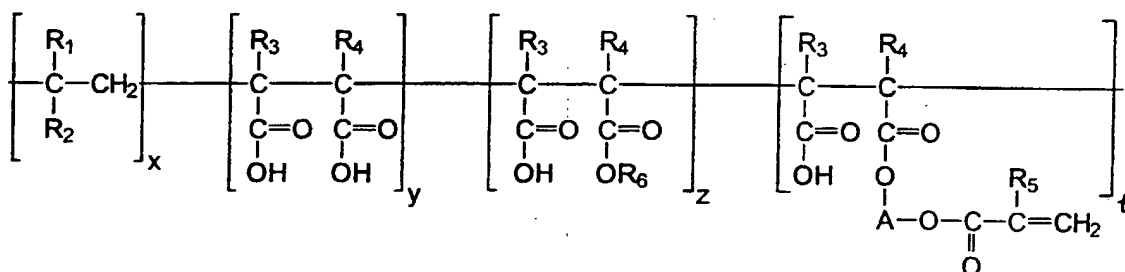
consideration of the present disclosure, that the invention is capable of numerous modifications, substitutions, rearrangements of parts and/or improvements without departing from the spirit and scope of the invention as set forth in the following claims.

What is claimed is:

1. An aqueous polymer dispersion comprising a polymer substantially free of cationic polymerizable groups and a cationic photoinitiator, wherein the polymer is capable of being precipitated by an acid generating photoinitiator upon exposure to radiation.

2. The aqueous polymer dispersion of Claim 1 wherein the polymer is selected from polyamide resins, acrylic resins, acrylated acrylic resins, amino resins, polyester resins, urethane resins, starch, polysulfonate resins, phenolic resins and melamine resins.

3. The aqueous polymer dispersion of Claim 1 wherein the polymer is an energy curable polymer having the general structure:



wherein:  $R_1$  and  $R_2$  are independently selected from the group consisting of hydrogen,  $C_1$ - $C_{20}$  alkyl,  $C_6$ - $C_{10}$  aryl,  $C_7$ - $C_{14}$  alkaryl,  $C_4$ - $C_{12}$  cycloalkyl and halogen such as chlorine, fluorine and bromine;  $R_3$ ,  $R_4$  and  $R_5$  are independently selected from the group consisting of hydrogen and  $C_1$ - $C_5$  alkyl;  $R_6$  is selected from the group consisting of alkyl, aralkyl, alkyl substituted aralkyl and oxyalkylated derivatives of same containing 2 to 4 carbon atoms in each oxyalkylene group, which group may be 1 to 20 and preferably 1 to 6 repeating units; A is a linear or branched divalent  $C_1$ - $C_{20}$  alkylene or oxyalkylated derivative thereof as described in connection with



$R_6$ ; and subscripts  $x$ ,  $y$ ,  $z$  and  $t$  are whole numbers such that the sum of  $x$ ,  $y$ ,  $z$  and  $t$  ranges from 3 to 20, with each being equal to or greater than 1.

4. The aqueous polymer dispersion of Claim 1 wherein the acid generating photoinitiator is selected from diazonium salts; sulfonium salts; iodonium salts; ferrocinium salts; tetraphenylphosphonium tetrafluorophosphate; phenanthrolium bis-hexafluorophosphate; diphenylsulfoxonium hexafluorophosphate; triphenylselenonium salts; triphenyltelluronium salts; 2,6-diphenyl-4-*p*-chloro phenylthiopyryliumtetrafluoroborate; and cyclopentadienyl isopropylbenzene Iron (II).

5. The diazonium salts in Claim 4 selected from 2,5-diethoxy-4-(*p*-tolylmercapto)benzene diazonium hexafluorophosphate, 2,4,6-trichlorobenzene diazonium hexafluorophosphate, 2,4,6-tribromobenzene diazonium hexafluorophosphate, *p*-chloro benzenediazonium and hexafluorophosphate.

6. The sulfonium salts in Claim 4 selected from triarylsulfoniumhexafluorophosphate and triarylsulfonium hexafluoroantimonate.

7. The iodonium salts in Claim 4 selected from diphenyliodoniumhexafluorophosphate, diphenyliodonium hexafluoroarsenate, diphenyliodoniumtrifluoromethane sulfonate, diaryliodoniumtrifluoromethane sulfonate and UV 9310-C (available from GE Silicones, Waterford, NY).

8. The aqueous polymer dispersion of Claim 3 wherein  $R_1$  and  $R_2$  are independently selected from hydrogen, methyl, phenyl, benzyl, and  $C_4$ - $C_6$  cycloalkyl.

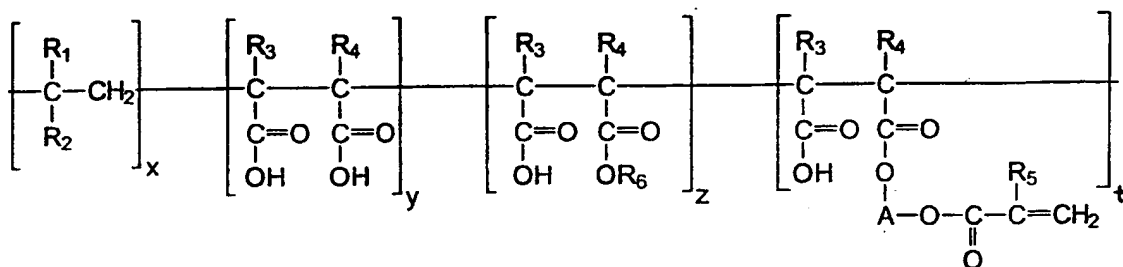
9. The polymer dispersion of Claim 3 wherein  $R_3$ ,  $R_4$  and  $R_5$  are independently selected from hydrogen and methyl.

10. A water based coating composition comprising:  
(i) the aqueous polymer dispersion of Claim 1; (ii) an

acid generating photoinitiator; and (iii) a free radical photoinitiator.

11. The coating of Claim 10 wherein the polymer is selected from polyamide resins, acrylic resins, acrylated acrylic resins, amino resins, polyester resins, urethane resins, starch, polysulfonate resins, phenolic resins and melamine resins.

12. The coating of Claim 10 wherein the polymer is an energy curable polymer having the general structure:



wherein:  $R_1$  and  $R_2$  are independently selected from the group consisting of hydrogen,  $C_1$ - $C_{20}$  alkyl,  $C_6$ - $C_{10}$  aryl,  $C_7$ - $C_{14}$  alkaryl,  $C_4$ - $C_{12}$  cycloalkyl and halogen such as chlorine, fluorine and bromine;  $R_3$ ,  $R_4$  and  $R_5$  are independently selected from the group consisting of hydrogen and  $C_1$ - $C_5$  alkyl;  $R_6$  is selected from the group consisting of alkyl, aralkyl, alkyl substituted aralkyl and oxyalkylated derivatives of same containing 2 to 4 carbon atoms in each oxyalkylene group, which group may be 1 to 20 and preferably 1 to 6 repeating units; A is a linear or branched divalent  $C_1$ - $C_{20}$  alkylene or oxyalkylated derivative thereof as described in connection with  $R_6$ ; and subscripts x, y, z and t are whole numbers such that the sum of x, y, z and t ranges from 3 to 20, with each being equal to or greater than 1.

13. The coating composition of Claim 10 wherein the acid generating photoinitiator is selected from diazonium salts; sulfonium salts; iodonium salts; ferrocenium salts;

tetraphenylphosphonium tetrafluorophosphate; phenanthrolium bis-hexafluorophosphate; diphenylsulfoxonium hexafluorophosphate; triphenylselenonium salts; triphenyltelluronium salts; 2,6-diphenyl-4-p-chlorophenylthiopyryliumtetrafluoroborate; and cyclopentadienyl isopropylbenzene Iron (II).

14. The coating composition of Claim 13 wherein the diazonium salts are selected from 2,5-diethoxy-4-(p-tolylmercapto)benzene diazonium hexafluorophosphate, 2,4,6-trichlorobenzene diazonium hexafluorophosphate, 2,4,6-tribromobenzene diazonium hexafluorophosphate, p-chloro benzenediazonium and hexafluorophosphate.

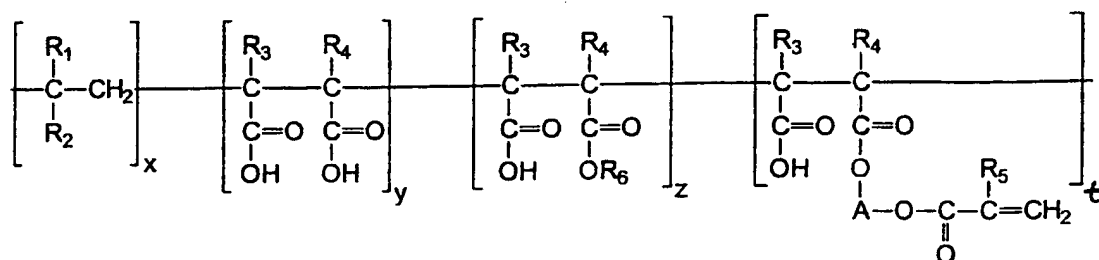
15. The coating composition of Claim 13 wherein the sulfonium salts are selected from triarylsulfoniumhexafluorophosphate and triarylsulfonium hexafluoroantimonate.

16. The coating composition of Claim 13 wherein the iodonium salts are selected from diphenyliodoniumhexafluorophosphate, diphenyliodonium hexafluoroarsenate, diphenyliodoniumtrifluoromethane sulfonate, diaryliodoniumtrifluoromethane sulfonate and UV 9310-C (available from GE Silicones, Waterford, NY).

17. A water based printing ink composition comprising: (i) the aqueous polymer dispersion of Claim 1; (ii) an acid generating photoinitiator; (iii) a free radical photoinitiator; and (iv) a pigment.

18. The printing ink of Claim 17 wherein the polymer is selected from polyamide resins, acrylic resins, acrylated acrylic resins, amino resins, polyester resins, urethane resins, starch, polysulfonate resins, phenolic resins and melamine resins.

19. The printing ink of Claim 17 wherein the polymer is an energy curable polymer having the general structure:



wherein:  $R_1$  and  $R_2$  are independently selected from the group consisting of hydrogen,  $C_1$ - $C_{20}$  alkyl,  $C_6$ - $C_{10}$  aryl,  $C_7$ - $C_{14}$  alkaryl,  $C_4$ - $C_{12}$  cycloalkyl and halogen such as chlorine, fluorine and bromine;  $R_3$ ,  $R_4$  and  $R_5$  are independently selected from the group consisting of hydrogen and  $C_1$ - $C_5$  alkyl;  $R_6$  is selected from the group consisting of alkyl, aralkyl, alkyl substituted aralkyl and oxyalkylated derivatives of same containing 2 to 4 carbon atoms in each oxyalkylene group, which group may be 1 to 20 and preferably 1 to 6 repeating units; A is a linear or branched divalent  $C_1$ - $C_{20}$  alkylene or oxyalkylated derivative thereof as described in connection with  $R_6$ ; and subscripts x, y, z and t are whole numbers such that the sum of x, y, z and t ranges from 3 to 20, with each being equal to or greater than 1.

20. The printing ink of Claim 17 wherein the acid generating photoinitiator is selected from diazonium salts; sulfonium salts; iodonium salts; ferrocinium salts; tetraphenylphosphonium tetrafluorophosphate; phenanthrolium bis-hexafluorophosphate; diphenylsulfoxonium hexafluorophosphate; triphenylselenonium salts; triphenyltelluronium salts; 2,6-diphenyl-4-p-chloro phenylthiopyryliumtetrafluoroborate; and cyclopentadienyl isopropylbenzene Iron (II).

21. The printing ink of Claim 20 wherein the diazonium salts are selected from 2,5-diethoxy-4-(p-tolylmercapto)benzene diazonium hexafluorophosphate, 2,4,6-trichlorobenzene diazonium hexafluorophosphate,

2,4,6-tribromobenzene diazonium hexafluorophosphate, p-chloro benzenediazonium and hexafluorophosphate.

22. The coating composition of Claim 20 wherein the sulfonium salts are selected from triarylsulfoniumhexafluorophosphate and triarylsulfonium hexafluoroantimonate.

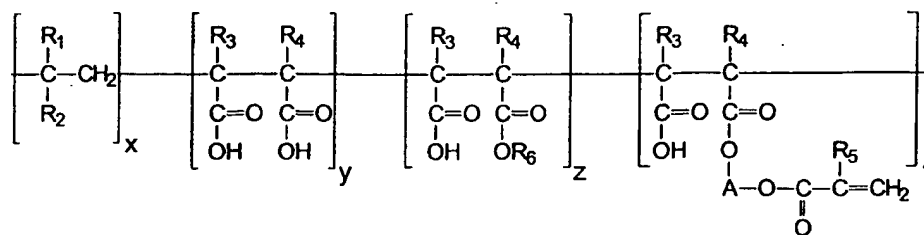
23. The coating composition of Claim 20 wherein the iodonium salts are selected from diphenyliodoniumhexafluorophosphate, diphenyliodonium hexafluoroarsenate, diphenyliodoniumtrifluoromethane sulfonate, diaryliodoniumtrifluoromethane sulfonate and UV 9310-C (available from GE Silicones, Waterford, NY).

24. An aqueous polymer dispersion comprising a polymer substantially free of cationic polymerizable groups and a cationic photoinitiator, wherein the polymer is capable of being precipitated by a base generating photoinitiator upon exposure to radiation.

25. The aqueous polymer dispersion of Claim 25 wherein the base generating photoinitiator is selected from carbamates, oximes, inorganic amines, and complexes of the general structure  $\text{Co}(\text{NH}_2\text{Z}_5)(\text{K})_n$  where Z is a methyl or n-propyl group, K is chloride, bromide or perchlorate ion and n is an integer from 1 to 2.

26. The aqueous polymer dispersion of Claim 24 wherein the polymer is selected from polyamide resins, acrylic resins, acrylated acrylic resins, amino resins, polyester resins, urethane resins, starch, polysulfonate resins, phenolic resins and melamine resins.

27. The aqueous polymer dispersion of Claim 24 wherein the polymer is an energy curable polymer having the general structure:



wherein:  $R_1$  and  $R_2$  are independently selected from the group consisting of hydrogen,  $C_1$ - $C_{20}$  alkyl,  $C_6$ - $C_{10}$  aryl,  $C_7$ - $C_{14}$  alkaryl,  $C_4$ - $C_{12}$  cycloalkyl and halogen such as chlorine, fluorine and bromine;  $R_3$ ,  $R_4$  and  $R_5$  are independently selected from the group consisting of hydrogen and  $C_1$ - $C_5$  alkyl;  $R_6$  is selected from the group consisting of alkyl, aralkyl, alkyl substituted aralkyl and oxyalkylated derivatives of same containing 2 to 4 carbon atoms in each oxyalkylene group, which group may be 1 to 20 and preferably 1 to 6 repeating units; A is a linear or branched divalent  $C_1$ - $C_{20}$  alkylene or oxyalkylated derivative thereof as described in connection with  $R_6$ ; and subscripts  $x$ ,  $y$ ,  $z$  and  $t$  are whole numbers such that the sum of  $x$ ,  $y$ ,  $z$  and  $t$  ranges from 3 to 20, with each being equal to or greater than 1.

12

# EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

21 Application number: 80901622.3

51 Int. Cl.<sup>3</sup>: G 03 C 1/68

22 Date of filing: 28.08.80

C 08 F 2/48, C 08 L 35/06  
 G 09 F 7/00

Data of the international application taken as a basis:

86 International application number:  
PCT/JP80/00198

87 International publication number:  
WO81/00626 (05.03.81 81/06)

30 Priority: 28.08.79 JP 108570/79

43 Date of publication of application:  
16.09.81 Bulletin 81/37

84 Designated Contracting States:  
DE FR GB

71 Applicant: ARAI, Tokuji  
14, 1-chome, Yamato-cho Naka-ku, Yokohama-shi  
Kanagawa 232(JP)

71 Applicant: TAKLE, Birger  
Kjöiavei 39  
NO-1370 Asker(NO)

71 Applicant: Takaki, Kiyofumi  
2-13, Kitahonmachi 4-chome Yao-shi  
Osaka 581(JP)

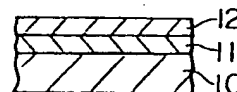
72 Inventor: TAKAKI, Kiyofumi  
2-13, Kitahonmachi 4-chome Yao-shi  
Osaka 581(JP)

74 Representative: Patentanwälte  
Henkel-Kern-Feiler-Hänzel  
Möhlstrasse 37  
D-8000 München 80(DE)

## 54 PHOTO-POLYMERIZABLE LIGHT-SENSITIVE RESIN COMPOSITION AND LIGHT-SENSITIVE SHEET MATERIAL

57 Photo-polymerizable light-sensitive resin composition containing a styrene/maleic acid copolymer resin, an ethylenically unsaturated compound, and a photo-polymerization initiator. A light-sensitive sheet comprising support (10) having a layer (11) of said photo-polymerizable light-sensitive resin composition is also disclosed. The composition and the sheet material can be advantageously used particularly for preparing various cards such as credit cards and cash cards.

Fig. 1



DESCRIPTION**TITLE MODIFIED**

see front page

## TITLE OF THE INVENTION

Photopolymerizable Radiation-sensitive Resin Composition and Radiation-sensitive Sheet Material

## TECHNICAL FIELD

5 The present invention relates to a photopolymerizable radiation-sensitive resin composition and a radiation-sensitive sheet material comprising a layer of such composition. In particular, the present invention relates to a photopolymerizable radiation-sensitive resin composition  
10 and a radiation-sensitive sheet material comprising a layer of such composition, which are suitable for use in the preparation of identification cards (so-called ID cards) and the other similar cards having encapsulated therein a photographic image.

## 15 BACKGROUND ART

With the advance of information processing by means of computers, various cards having a magnetic coating are frequently used as an input medium to an input device of the computer. For example, typical cards include a credit  
20 card, a banking or cash card, a driver's licence card, a commutation or season ticket, a key card and the like. In these cards which have special usages, the requirements concerning the quality of the material and the construction imposed on them are widely varied. For instance, in accordance with the standards provided by the Japanese  
25 Banker's Association and the American Banker's Association, credit cards and banking or cash cards should have a base sheet of vinyl chloride resin. Furthermore, it is generally well-known that from the view point of crime prevention, such care must be taken that the cards may not easily be  
30 forged or falsified and may not unjustly be used by any person other than the owner. These aims which are very desirable to prevent crime and other related aims are best achieved by, for example, reproducing a photograph of the  
35 owner's face and or a signature of the owner on the surface



of the base sheet of the card and furthermore covering the reproduction with a protective sheet. However, in order to realize the above aims, it is necessary to first solve several technical problems. Examples of the problems to be solved are that the reproduced photograph or signature should be clear and fine and be easily discriminable and that the protective sheet should be firmly adhered to the base sheet. Furthermore, it will be understood, if the use of the card as an input medium to an input device of a computer is considered, that the card should not be deformed and the surface of the card must not lose its smoothness. However, in fact, it is very troublesome to form an image having a beautiful color and an excellent discrimination quality on the base sheet. For example, since cards of this type have different patterns to be reproduced on the card, it is difficult and expensive to attain a precise reproduction of the patterns through a printing process. Furthermore, since the reproduction is interposed between the base sheet and the protective sheet, it is necessary to take care so that the bonding of these sheets will not be undesirably affected.

It has long been effected in the formation of a person's photograph and signature on the base sheet to reproduce photographically such a photograph and signature, and it has also been well-known that various radiation-sensitive resins can be used for this object. One of the well-known radiation-sensitive resins includes diazo compounds. The diazo compounds are generally radiation-sensitive resins which are obtained by mixing a water-soluble colloidal material such as gelatin, polyvinyl alcohol, casein, emulsified polyvinyl acetate and the like, with the diazo compounds. A process for the production of cards using the above-mentioned radiation-sensitive resins comprises coating a radiation-sensitive resin on a base sheet, and exposing it to actinic radiation through a transparent negative to water-insolubilize the radiation-sensitive resin in areas exposed to radiation, namely, the exposed

areas. Then, the radiation-sensitive resin in the un-exposed areas on the base sheet is removed through washing with water. Thereafter, a hardened image formed on the exposed areas is dyed. While this process can provide an  
5 image having any desired colour, it suffers from such a drawback that the dyes used in dyeing of the image tend to stain the base sheet. This well-known process for the production of the cards has further drawbacks that the radiation-sensitive resins used therein have a poor shelf  
10 stability (due to their reaction in the dark) and therefore, if they are used, they must be coated on the base sheet immediately before exposure to radiation. The drawbacks similar to those can be caused even if the diazo compounds are replaced with bicromates or iron salts.

15 It has been well-known that radiation-sensitive resins containing diazo compounds and couplers corresponding thereto are also useful in the preparation of the cards. The well-known process for the production of cards using the above radiation-sensitive resins comprises exposing a  
20 radiation-sensitive resin-containing coating formed on a base sheet to an actinic radiation through a transparent negative, and colour developing the exposed coating in an alkaline aqueous solution or gaseous ammonia. However, this process has drawbacks in that only a few colours are  
25 usable in dyeing the images due to a limited combination of the diazo compounds and the couplers. Furthermore, this process involves undesired problems that the unexposed areas are also slightly coloured.

As another process using diazo compounds, a radiation-sensitive resin comprising a blend of the diazo compounds  
30 and pigments is also well-known. Sheet structures having a coating of such a radiation-sensitive resin are disclosed, for example, in the U.S. Patent Application filed on November 26, 1958 (Assignee: Minnesota Mining and  
35 Manufacturing Company). The base sheet used in this U.S. application is a metal base sheet which is suitable as a printing master plate. However, even if the base sheet is

replaced with one composed of vinyl chloride resins, desirable results cannot be obtained. This is because, when a diazo-type radiation-sensitive resin is coated on the base sheet composed of vinyl chloride resins, some chemical modification can be caused on the surface portion of the base sheet. The chemical modification results in marrying the unexposed areas of the base sheet. Especially, when a pigment is contained in the radiation-sensitive resin, the pigment is adsorbed onto the base sheet prior to exposure to radiation. Therefore, even after the removal of the radiation-sensitive resin in the unexposed areas as a result of development, a stain on the base sheet due to the adsorbed pigment can not be removed and remains indelible. Apparently, this is because any organic solvent which will dissolve vinyl chloride resins, such as toluene, xylene, methyl ethyl ketone, cyclohexane, acetone, ethyl acetate and the like, must be used in the radiation-sensitive resin composition. The chemical modification in the surface of the base sheet results in, in addition to the marrying mentioned above, difficulties in adhering a protective film to the surface of the base sheet through heat fusion. These drawbacks are very undesirable in the production of the cards, but the cause or causes have not yet been clarified.

It is also known to produce a coloured image on the base sheet using a silver salt emulsion. For example, this process is a dye transfer process developed by Eastman Kodak Company. According to this imaging process, a silver salt matrix film (Trade name: KODAK Dye Transfer Film) is firstly imagewise exposed with a tungsten lamp through a transparent negative. Then, the exposed film is developed with a developing solution to harden gelatin in the exposed areas of the film, and the unexposed areas of the film are washed off with warm water. Thereafter, the exposed areas are dyed with a dye, and the dyed image is transferred to a base sheet. Thus, a coloured image can be formed on the base sheet. However, the coloured image obtained through

the above imaging process has drawbacks in that, if in the subsequent processing steps a protective coating is formed on the base sheet or a protective sheet is laminated on the base sheet, the coloured image bleeds out. Further, the matrix film which was used in the transfer process must be discarded due to nonuse in the subsequent steps, and this means that the use of the matrix film is not economical. In addition to the above process, a process which comprises directly adhering a matrix film of the above-mentioned type, the unexposed areas of which can be washed off, to the base sheet is also proposed. According to this process, the exposed and developed matrix film can be blackened with a blackened silver bleaching solution containing as a main component potassium ferrocyanide and the like, and, after bleaching the film, the bleached portion of the film can be dyed to obtain a coloured image having any desired colour. Accordingly, the thus obtained film can be bonded to the base sheet by means of a special adhesive to form any desired coloured image on the base sheet. This process would be economical since the matrix film used herein also functions as the laminate film. However, the cards produced in accordance with this process are likely to undergo deformation or become crooked because the quality of the matrix film is different from that of the base sheet. Furthermore, potassium ferrocyanide used in the bleaching step is likely to cause water pollution problems, since the solution containing waste potassium ferrocyanide is decomposed by ultra violet radiations in sun light to form toxic cyanogen.

Various radiation-sensitive resins are further well-known. For example, Japanese Patent Publication Gazette No. 45-022,085 discloses the radiation-sensitive resins containing polyazide vinyl benzoate, and those containing cinnamic acid esters and the like. However, most of these radiation-sensitive resins cannot be coated on the base sheet composed of vinyl chloride resins, since an organic solvent which may dissolve the base sheet is contained

either in the radiation-sensitive resins or in the developing solution which is used in the subsequent processing.

The inventors, aware of the above information, made efforts to develop a suitable photopolymerizable radiation-sensitive resin composition for forming photographic  
5 images, which has not the drawbacks mentioned above. As a result of this, we found the following photopolymerizable radiation-sensitive resin compositions.

(A) A photopolymerizable composition which is soluble  
10 in water or weak alkaline aqueous solution, the composition comprising different polymerizable polymers such as polymers of polyester type, polyacryl type, polyurethane type, polyamide type or cellulose type, those containing double bonds in its molecule, those having been modified and the  
15 like, a crosslinking agent (binding agent), and a photoreaction initiator;

(B) A photopolymerizable composition which comprises polymerizable monomers, a binding agent soluble in water or weak alkaline aqueous solution, and a photoreaction  
20 initiator, and;

(C) A photopolymerizable composition which comprises polymerizable oligomers, a binding agent soluble in water or weak alkaline aqueous solution, and a photoreaction initiator.

However, these polymerizable radiation-sensitive resin  
25 compositions can not show a practically useful sensitivity without adding thereto a suitable photopolymerization initiator, since their photopolymerization proceeds slowly. In order to attain a practically useful photopolymerization rate, different photopolymerization initiators must be  
30 added to the composition, as its essential component, separately or in combination of two or three initiators depending upon the particular radiation-sensitive resin composition to be used. However, these photopolymerizable compositions cause a dark reaction under the influence of  
35 heat and the like, are gradually polymerized, and become insoluble in a solvent. In addition, such a reaction is generally further accelerated through the addition of the

photopolymerization initiator. Generally, for the purpose of inhibiting polymerization caused during keeping or producing under the influence of heat and the like, various polymerization inhibitors are added to the photopolymerizable compositions to improve their shelf stability. 5 However, while the addition of suitable polymerization initiators is effective to improve the shelf stability of the photopolymerizable compositions, it also has drawbacks in that the photopolymerizability of the compositions is 10 inhibited. Therefore, the amount of the polymerization initiators to be added is necessary to be remarkably small.

The photopolymerizable compositions which can effect only a limited photopolymerization and show a low rate of hardening are not preferable as the composition for use in 15 the production of credit cards. This is because it is difficult to reproduce an image having excellent sharpness from compositions with a low hardening rate, since such compositions need a long exposure time to attain an image-wise exposure for imaging. In this connection, a method of 20 shortening the exposure time, which comprises increasing the amount of radiation energy emitted from the exposure light source, is proposed. However, in practicing this method, we must allow for remarkable exothermic heat produced at the same time. For example, when a substrate 25 such as a sheet of vinyl chloride is used, the heat from the light source will cause undesirable results such as a deformation and modification of the substrate and the like.

#### DISCLOSURE OF THE INVENTION

It is an object of the present invention to provide a 30 novel photopolymerizable radiation-sensitive resin composition which can completely eliminate the above-discussed drawbacks of the prior radiation-sensitive resins.

It is another object of the present invention to provide a photopolymerizable radiation-sensitive resin 35 composition which does not contain an organic solvent capable of dissolving, particularly, vinyl chloride or vinyl chloride-vinyl acetate copolymeric resins.

Furthermore, it is another object of this invention to provide a photopolymerizable radiation-sensitive resin composition which is soluble in water or a highly diluted alkaline aqueous solution and in which the dissolved components can be easily recovered through neutralization.

In addition, it is another object of this invention to provide a photopolymerizable radiation-sensitive resin composition in which pigments may be freely incorporated depending upon the desired hue.

In addition, it is another object of this invention to provide a photopolymerizable radiation-sensitive resin composition which is photopolymerized by ultraviolet radiation having wavelengths of from 2,500 to 4,200 Å and is not photopolymerized by radiation having wavelengths of more than 4,200 Å, and therefore which may be subjected to an exposure step under daylight conditions.

In addition, it is another object of this invention to provide a photopolymerizable radiation-sensitive resin composition having a long-term shelf stability.

A further object of the invention is to provide a radiation-sensitive sheet material having a water-soluble or weak alkali-soluble protective coating formed on a layer of radiation-sensitive material, in which the protective coating does not inhibit a photopolymerization of radiation-sensitive resin which is induced by actinic radiation irradiated onto the layer of radiation-sensitive material, and does not chemically bond with the photopolymerized resin during photopolymerization of the radiation-sensitive resin.

According to the present invention, there is provided a photopolymerizable radiation-sensitive resin composition comprising a styrene-maleic acid copolymeric resin as well as an ethylenically unsaturated compound and a photopolymerization initiator.

Also, according to the present invention, there is provided a radiation-sensitive sheet material comprising a support and, at least, a layer of a radiation-sensitive

material coated on one side of the support, said layer of the radiation-sensitive material being a layer of a photopolymerizable radiation-sensitive resin composition which comprises a styrene-maleic acid copolymeric resin as well  
5 as an ethylenically unsaturated compound and a photopolymerization initiator.

According to this invention, the sheet material having sensitivity can be obtained, and the surface of the obtained sheet material has an excellent abrasion resistance. When  
10 the sheet material is conventionally exposed to an actinic radiation and then washed with water or a weak alkaline aqueous solution, an overall protective coating formed on the sheet material and an unexposed radiation-sensitive material lying under the protective coating can be  
15 completely removed. Thus, only an image which is formed from the insoluble radiation-sensitive material existing within the exposed areas of the sheet material is sharply produced. While the surface of the support, which surface lies under the insoluble radiation-sensitive material, can  
20 be firmly bonded to said insoluble radiation-sensitive material, the other surface of the support is not changed and is as before. Therefore, it is possible to firmly bond a protective sheet to the support to protect the image formed on the support.

25 BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings will be briefly described. In these drawings:

Figure 1 is a cross-sectional view of the radiation-sensitive sheet material according to the present  
30 invention, which comprises a layer of the photopolymerizable radiation-sensitive resin composition and a protective coating,

Figure 2 is a cross-sectional view of the radiation-sensitive sheet material as is shown in Figure 1,  
35 which has been exposed to an actinic radiation, and

Figure 3 is a cross-sectional view of the exposed sheet material as is shown in Figure 2, which has been



processed with a processing solution.

#### BEST MODE FOR CARRYING OUT THE INVENTION

The photopolymerizable radiation-sensitive resin compositions according to the present invention comprise  
5 polymers which are photopolymerizable and alkali-soluble. As the polymers of this type, for example, novolak type phenol-formaldehyde resins, copolymers of acrylic or methacrylic acid, alkyd resins having a high acid value, shellac-acrylic acid copolymers, styrene-maleic acid co-  
10 polymeric resins and the like are well-known. Among these polymers, particular styrene-maleic acid copolymeric resins are selected and used in the present invention. The reason why the above particular polymers are used in the present invention is based on the following facts. Namely, while  
15 the styrene-maleic acid copolymeric resin is photopolymerized by actinic radiation in the presence of a photopolymerization initiator and, as a result of this, its inherent alkali-solubility is lost, the unpolymerized styrene-maleic acid copolymeric resin, when it has added  
20 thereto an unsaturated compound with a polymerizable ethylene bond, its alkali-solubility is increased greatly. Accordingly, the polymer having added thereto an unsaturated compound can be dissolved with alkali weaker than that used in dissolving the polymer, comprising only styrene-maleic  
25 acid copolymeric resin having no unsaturated compound added thereto, and the photopolymerization initiator. Although many similar experiments were repeated using other polymers, an alkali-solubility which was equivalent to or more than that of the above-mentioned styrene-maleic acid copolymeric  
30 resin could not be attained.

Styrene-maleic acid copolymeric resins which are copolymeric resins of styrene and maleic anhydride are widely used in many applications such as paints, sizing agents for textiles, aqueous printing inks and  
35 the like. These resins are commercially available, e.g., from Sinclair Petrochemicals, Inc. under the trade name: SMA Resin, from Monsanto Chemical Co. under the

trade name: LYTRON Resin, and from Daido Industrial Co., Ltd. under the trade name: Stylite, respectively. The styrene-maleic acid copolymeric resins generally have a molecular weight of from 700 to 50,000. The molecular weight varies depending upon various factors such as amounts of monomers used in the production of the copolymeric resins, reaction period of time, degree of esterification and the like. Furthermore, the acid value of these copolymeric resins usually ranges from 130 to 500. The styrene-maleic acid copolymeric resins useful in embodying the present invention have a molecular weight of from 1,000 to 2,000 and an acid value of from 130 to 220. Styrene-maleic acid copolymeric resins, which are partially esterified styrene-maleic anhydride resins and contain carboxyl groups yet remaining in the molecule, are particularly preferred.

The following Table I illustrates the results which are obtained when the amount of an ethylenically unsaturated compound to be added to the styrene-maleic acid copolymeric resin is widely varied. It will be understood from this table that the alkali-solubility of the styrene-maleic acid copolymeric resin is more and more increased with the increase in the amount of the unsaturated compound added thereto. In the Table I below, all parts used herein are by weight, and alkali used herein is a 0.0005% solution of anhydrous sodium carbonate. The thickness of the dried coating is 10 microns.

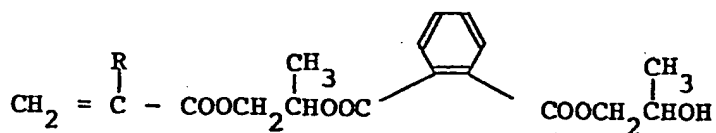
Table I

<u>Styrene-maleic acid copolymeric resin</u>	<u>Unsaturated compound</u>	<u>Initiator</u>	<u>Speed of development</u>	<u>Unexposed coating</u>	<u>Exposed and developed coating</u>
94 parts	0	6 parts	more than 180"	hard, non-tacky	hard, non-tacky, cracks when bent
80 parts	14 parts	6 parts	60" - 90"	hard, non-tacky	hard, non-tacky, slightly poor solvent resistance
72 parts	22 parts	6 parts	35" - 45"	hard, non-tacky	hard, non-tacky, good coating
64 parts	30 parts	6 parts	30" - 40"	hard, non-tacky	hard, good coating
58 parts	36 parts	6 parts	20" - 30"	hard, non-tacky	hard, good coating
52 parts	42 parts	6 parts	15" - 25"	slightly hard, slightly tacky	slightly brittle, cracks when bent
35 parts	59 parts	6 parts	10" - 20"	soft, tacky	brittle, easily cracks

The ethylenically unsaturated compounds useful in the present invention are polymerizable compounds which contain one or more ethylenically unsaturated double bonds in one molecule thereof. The term "ethylenic compounds", when  
 5 used herein, is intended to mean the compounds (including monomers, prepolymers, dimers, trimers and other oligomers) which contain at least one ethylenically unsaturated double bond in their chemical structure.

The ethylenic compound which is advantageously usable  
 10 in embodying the present invention is a mixture of (A) one or more ethylenic compounds (with a terminal hydroxyl group) having a molecular weight of 150 or more and a boiling point, under normal pressure, of 100°C or more and containing at least one acryloyl or methacryloyl group, and  
 15 (B) one or more ethylenic compounds having a molecular weight of 150 or more and a boiling point, under normal pressure, of 100°C or more and containing at least one acryloyl or methacryloyl group.

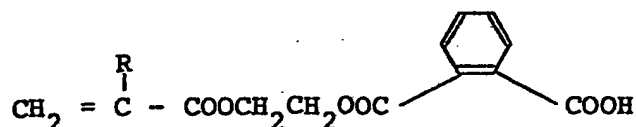
Examples of the above-mentioned ethylenic compounds  
 20 (A) include, for example, polyester monoacrylate represented by the structural formula:



where R is H or CH<sub>3</sub>, 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, 1,4-butylene glycol monoacrylate and the like.

Examples of the above-mentioned ethylenic compounds  
 30 (B) include, for example, polyethylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butylene glycol diacrylate, 1,6-hexane glycol diacrylate, neopentyl glycol diacrylate, 2,2-bis (4-acryloxy diethoxy phenyl) propane, 2,2-bis (4-acryloxy propyloxy phenyl) propane, trimethylol  
 35 propane triacrylate, tetramethylol methane triacrylate, ethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, 1,6-hexane glycol dimethacrylate, polypropylene

glycol dimethacrylate, 2,2-bis (4-methacryloxy ethoxy phenyl) propane, 2,2-bis (4-methacryloxy diethoxy phenyl) propane, trimethylol propane trimethacrylate, polyester acrylate oligomer, polyamide acrylate, epoxy acrylate, 5 polyurethane acrylate, polyester monoacrylate represented by the structural formula:



wherein R is H or CH<sub>3</sub>, and the like.

Examples of the photopolymerization initiators usable in the present invention are, for example, one or more compounds selected from the group consisting of acyloin such 15 as benzoin and the like; acyloin derivatives such as benzoin methyl ether, benzoyl ethyl or isopropyl or benzoin isobutyl ether and the like; ketones such as benzophenone, acetophenone, methyl ethyl ketone, benzyl and the like; substituted benzophenones such as Michler's ketone, halogenated 20 benzophenone and the like; aldehydes such as benzaldehyde, dimethyl amino benzaldehyde, 4-hydroxy-3-methoxy benzaldehyde, naphthal-aldehyde, cinnamaldehyde and the like, and; substituted or unsubstituted polynuclear quinones such as xanthone, 3-chloroxanthone, 3,9-dichloroxanthone, anthra- 25 quinone, 1-chloroanthraquinone, 2-ethylanthraquinone, 1,4-naphthoquinone and the like.

In the radiation-sensitive resin compositions according to the present invention, various pigments may be optionally incorporated therein depending upon the desired hue. As 30 typical examples of useful pigments, for example, the following compounds can be mentioned. However, the present invention should not be restricted to these compounds:

Yellow pigments:

35 Benzidine yellow, hansa yellow, chrome yellow and the like

Red pigments:

Brilliant carmine, permanent reds, lithol

- 15 -

rubine, watchung red and the like

Blue pigments:

Phthalocyanine blue, alkali blue and the like

5 Black pigments:

Carbon black, iron black and the like.

In addition to these pigments, finely divided silicic acid may be used as a filler or a viscosity modifier.

The photopolymerizable radiation-sensitive resin  
10 composition in accordance with the invention comprises a styrene-maleic acid copolymeric resin as an alkali-soluble polymer as well as 10 through 60% by weight, based on the weight of said copolymeric resin, of ethylenically unsaturated compound and 1 through 10% by weight, based on  
15 the total weight of the copolymeric resin and the ethylenically unsaturated compound, of the photopolymerization initiator. With regard to the ethylenically unsaturated compound, it is further added that a ratio, of percentage by weight, of the compound (A) having a molecular weight of  
20 150 or more, a boiling point, under normal pressure, of 100°C or more, at least one acryloyl or methacryloyl group, and a terminal hydroxyl group to the compound (B) having a molecular weight of 150 or more, a boiling point, under normal pressure, of 100°C or more, and at least one acryloyl  
25 or methacryloyl group is 40 through 60%. If the above ethylenic compound (B) is used in an amount which is less than the lower limit of the above range, drawbacks such as delay of photopolymerization and the like will be caused. On the other hand, if the ethylenic compound (B) is used in  
30 an amount more than the upper limit of the above range, drawbacks such as insufficient adhesion of the photocured coating to vinyl chloride and the like will result.

In the photopolymerizable radiation-sensitive resin composition of the present invention, it is preferred that  
35 benzyl and dimethyl amino benzaldehyde are selected as the photopolymerization initiator among the above-listed photopolymerization initiators, and they are optionally combined

and used so that a ratio, of percentage by weight, of dimethyl amino benzaldehyde to benzyl is within the range of from 10 to 90%. The use of a combination of the photopolymerization initiators is preferred due to the following reasons. Namely, in the composition comprising the above-discussed styrene-maleic acid copolymeric resin having incorporated therein the ethylenic compound, the resulting rate of photopolymerization is remarkably slow and therefore a practically effective sensitivity can not be obtained if each of benzyl and dimethyl amino benzaldehyde is added separately to the composition, while a very fast rate of photopolymerization can be attained if benzyl and dimethyl amino benzaldehyde are used in combination and furthermore if they are combined at a specific ratio. In addition, it was found that, although the reasons have not yet been completely grasped, the radiation-sensitive resin composition of the present invention can be kept stably for a remarkably long duration without adding any shelf stabilizer such as a thermal polymerization inhibitor and the like, if a combination of benzyl and dimethyl amino benzaldehyde is used as the photopolymerization initiator. Though similar comparison was tried using other combinations of the photopolymerization initiators, notably excellent results, which were obtained when benzyl and dimethyl amino benzaldehyde were used in combination, could not be attained.

In the photopolymerizable radiation-sensitive resin composition in accordance with the present invention, if any pigment is added to the composition, it may be added thereto in an amount of 1 through 50 parts by weight based on the weight of the composition, and if any thermal polymerization inhibitor is added to the composition, it may be added thereto in an amount of 0.01 through 2% by weight based on the weight of the composition.

The photopolymerizable radiation-sensitive resin compositions in accordance with the present invention will be further described with reference to the following examples. While the examples mentioned below illustrate

the radiation-sensitive resin compositions which are suitable in the production of cards, it should be appreciated that these examples illustrate only one example of the present invention and they do not restrict the applications of the present invention and the compositions or proportions of the ingredients of the present invention. The "parts" used in the examples is intended to mean "parts by weight" unless otherwise stated.

Example 1-1

First group:

Styrene-maleic acid copolymeric resin	22 parts
Ethylene glycol monoethyl ether	20 parts

Second group:

Carbon black	3.5 parts
Phthalocyanine blue	0.5 parts

Third group:

2-hydroxy ethyl acrylate	7 parts
Trimethylol propane triacrylate	9 parts
Benzyl	1.6 parts
Dimethyl amino benzaldehyde	0.4 parts
Ethanol	36 parts

Firstly, the substances of the above-mentioned first group are added to a vessel equipped with a reflux condenser, and are dissolved while stirring at a temperature of 80 to 90°C. Heating is stopped after the substances added to the vessel are completely dissolved. Thereafter the solution is allowed to cool to room temperature while stirring. The resulting solution is transferred to a porcelain or stainless steel ball mill, wherein it is milled with the substances of the above-mentioned second group for a period of about 24 hours. Thereafter, the resulting mixture is transferred to a vessel equipped with a mixer or stirrer and the like, to which the substances of the above-mentioned third group are added. Stirring is continued for a period of about 2 hours. A black-coloured radiation-sensitive resin composition can be obtained.



Example 1-2

## First group:

	Styrene-maleic acid copolymeric resin	22 parts
5	2-hydroxy ethyl acrylate	9 parts

## Second group:

	2,2-bis (4-acryloxy diethoxy phenyl) propane	7 parts
	Benzyl	1.6 parts
10	Dimethyl amino benzaldehyde	0.4 parts

## Third group:

	Carbon black	3.5 parts
	Phthalocyanine Blue	0.5 parts
	Ethylene glycol monoethyl ether	36 parts
15	Ethanol	20 parts

First, the substances of the above-mentioned first group are added to a vessel equipped with a reflux condenser, and, while bubbling with air, are dissolved while stirring at a temperature of 130 to 140°. Heating is stopped after the substances added to the vessel are completely dissolved. The solution is cooled to a temperature of about 90°C while stirring and bubbling with air are further continued. Subsequently, the substances of the above-mentioned second group are added, and are stirred for about one hour. Thereafter, the resulting solution is transferred to a porcelain or stainless steel ball mill, to which the substances of the above-mentioned third group are then added and milled for a period of about 24 hours. A black-coloured radiation-sensitive resin composition can be obtained.

Example 1-3

## First group:

	Styrene-maleic acid copolymeric resin	22 parts
35	Polyester monoaligoacrylate having a terminal - OH group (Allonix M5700 commercially available from	9 parts

Toagosei Chemical Industry Co., Ltd.)

Second group:

5	Epoxy acrylate (Lipoxy VR80	7 parts
	commercially available from	
	Showa Koubunshi Kogyo Kabushiki	
	Kaisha)	
	Benzyl	1.6 parts
	Dimethyl amino benzaldehyde	0.4 parts

Third group:

10	Carbon black	3.5 parts
	Phthalocyanine Blue	0.5 parts
	Ethylene glycol monoethyl ether	36 parts
	Ethanol	20 parts

A radiation-sensitive resin composition is prepared in  
 15 accordance with the procedure similar to that as described  
 in Example 1-2.

Example 1-4

First group:

20	Styrene-maleic acid copolymeric	22 parts
	resin	
	2-hydroxy ethyl acrylate	9 parts

Second group:

25	Polyester monoooligoacrylate having	7 parts
	a terminal - COOH group (Allonix	
	M 8060.commercially available from	
	Toagosei Chemical Industry Co., Ltd.)	
	Benzyl	1.6 parts
	Dimethyl amino benzaldehyde	0.4 parts

Third group:

30	Carbon black	3.5 parts
	Phthalocyanine Blue	0.5 parts
	Ethylene glycol monoethyl ether	36 parts
	Ethanol	20 parts

A radiation-sensitive resin composition is prepared in  
 35 accordance with the procedure similar to that as described  
 in Example 1-2.

Example 1-5

## First group:

Styrene-maleic acid copolymeric resin	22 parts
Polyester monoooligoacrylate having	16 parts
a terminal - OH group	

## 5 Second group:

Benzyl	1.6 parts
Dimethyl amino benzaldehyde	0.4 parts

## Third group:

Carbon black	2.5 parts
Phthalocyanine Blue	0.5 parts
Ethylene glycol monoethyl ether	36 parts
Ethanol	20 parts

15 A radiation-sensitive resin composition is prepared in accordance with the procedure similar to that as described in Example 1-2.

Example 1-6

## First group:

Styrene-maleic acid copolymeric resin	22 parts
Ethylene glycol monoethyl ether	20 parts

## 20 Second group:

Carbon black	3.5 parts
Phthalocyanine Blue	0.5 parts

## Third group:

Polyurethane acrylate	16 parts
(Ubitan 788 commercially available from Thiokol Chemical Corp.)	
Benzyl	1.6 parts
Dimethyl amino benzaldehyde	0.4 parts
Ethanol	36 parts

30 A radiation-sensitive resin composition is prepared in accordance with the procedure similar to that described in Example 1-1.

Example 1-7

## First group:

Styrene-maleic acid copolymeric resin	22 parts
2,2-bis (4-acryloxy diethoxy phenyl)	16 parts

Ethylene glycol monethyl ether 10 parts

Second group:

Benzyl 1.6 parts

Dimethyl amino benzaldehyde 0.4 parts

5 Third group:

Carbon black 3.5 parts

Phthalocyanine Blue 0.5 parts

Ethylene glycol monoethyl ether 26 parts

Ethanol 20 parts

10 A radiation-sensitive resin composition is prepared in accordance with the procedure similar to that as described in Example 1-2.

Example 1-8

15 The procedure as described in Example 1-1 is repeated except that 2 parts of benzoin isopropyl alcohol is used in place of benzyl and dimethyl amino benzaldehyde in Example 1-1.

Example 1-9

20 The procedure as described in Example 1-3 is repeated except that 2 parts of benzoin isopropyl alcohol is used in place of benzyl and dimethyl amino benzaldehyde in Example 1-3.

Example 1-10

25 The procedure as described in Example 1-3 is repeated except that 2 parts of benzyl is separately used in place of benzyl and dimethyl amino benzaldehyde in Example 1-3.

30 The novel photopolymerizable radiation-sensitive resin composition according to the present invention will be generally usable after it is coated on a support. This is because the resulting coating is effective as a stable layer of radiation-sensitive material since its exposed areas are immediately insolubilized after exposure to radiation. Furthermore, it will be understood that the support to be laid under the layer of radiation-sensitive material may be made of vinyl chloride resins, since one or  
35 more solvents which cannot dissolve vinyl chloride or vinyl chloride-vinyl acetate copolymeric resins can be optionally

selected from the group consisting of alcohols, polyhydric alcohols and derivatives thereof as the solvent for use in the production of the radiation-sensitive resin composition according to the present invention. However, the materials  
5 of the support useful in the present invention also include, for example, paper, metals and the other conventional support materials. While the present invention has been described with respect to the application of its radiation-sensitive resin compositions in the production of cards,  
10 it should be appreciated that the radiation-sensitive resin compositions of the present application are also applicable to other technical fields in which known radiation-sensitive resin compositions are used.

The sheet material to which sensitivity is induced by  
15 the radiation-sensitive resin composition according to the present invention is illustrated in Figure 1 of the accompanying drawings. Figure 1 is a cross-sectional view of a support 10 having coated thereon a layer 11 of a soluble radiation-sensitive material. The radiation-sensitive resin  
20 composition which forms the layer 11 of the radiation-sensitive material has been already explained in detail. Generally, the layer 11 additionally contains a pigment. A protective coating 12 may be coated over the layer 11 of the radiation-sensitive material, as is the case with  
25 conventional photographic films. The protective coating 12 should be soluble in water or soluble in weak alkali, since the coating 12 is desirably removed with solvents for processing the layer 11. In this connection, it is  
30 necessary to take care to avoid such undesirable situations that the protective coating 12 will react with the layer 11 of the radiation-sensitive material and will become insoluble during storage.

The materials of the protective coating 12 which satisfy the above-mentioned requirements are, principally,  
35 water-soluble resins or alkali-soluble resins.

While it is well-known that the water-soluble resins include, for example, hydroxy ethyl cellulose, polyethylene

oxide, carboxymethylcellulose, polyvinyl alcohol and the like, it is particularly preferred that polyvinyl alcohol is used in embodying the present invention. Preferred polyvinyl alcohol is a partially saponified polyvinyl alcohol which has a degree of polymerization of from 1,000 to 1,500 and a degree of saponification of 80% or less. In the preparation of a protective coating-forming composition containing such water-soluble resin, the resulting composition generally contains 5 through 20% by weight, based on the weight of distilled water used as a solvent, of water-soluble resin, and further contains 0.5 through 5% by weight, based on the weight of the resultant solution, of a non-ionic surfactant or saponin. The non-ionic surfactant or saponin serves to prevent repellency between the layer 11 of the radiation-sensitive material and the protective coating 12 and to increase interfacial affinity therebetween, and, in addition to this, to improve the spreadability of the protective coating-forming composition during its application to form the coating 12. In some cases, the protective coating-forming composition may further contain 5 through 10% by weight, based on its weight, of finely divided silicic anhydride as a filler. Furthermore, in order to prevent focusing of the actinic radiation at the time of exposure, a pigment may be incorporated into the protective coating-forming composition. The pigment used herein is in an amount of 10 through 20% by weight, based on the weight of the solid water-soluble resin. Useful pigment is a water-dispersible pigment and is, for example, commercially available from Dainippon Ink & Chemicals, Inc. under the trade name: RIYU-DYE. Furthermore, a defoaming agent such as tributyl phosphate and the like is frequently used during the preparation of the protective coating-forming composition of the above-mentioned type. However, such a defoaming agent is not related to the composition of the protective coating itself.

The alkali-soluble resins have been already explained

in connection with the explanation of the radiation-sensitive resin composition. Examples of these resins include novolak type phenol-formaldehyde resins, copolymers of acrylic or methacrylic acid, alkyd resins having a high acid value, styrene-maleic acid copolymeric resins or its partially esterified resins, alkali salts of styrene-maleic acid copolymeric resins and the like. In order to embody the present invention, it is particularly preferred that the partially esterified products or alkali salts of styrene-maleic acid copolymeric resins are used as the alkali soluble resins. The above-mentioned alkali salts are commercially available from Monsanto Chemical Co., U.S.A., under the trade name: Stymer S Resin. Generally, in the preparation of a protective coating-forming composition containing the above alkali-soluble resin, 5 through 20% by weight, based on the weight of the solvent used, such as ethanol, ethylene glycol monoethyl ether acetate and the like, of the alkali-soluble resin is incorporated into the composition. Furthermore, if desired, finely divided silicic anhydride as a filler and a pigment as a focusing inhibitor may be incorporated into the composition, respectively, as is the case with the above-discussed protective coating-forming composition which contains a water-soluble resin.

The preparations of each of the above-mentioned water-soluble protective coating-forming compositions and alkali-soluble protective coating-forming compositions will be further described with reference to their typical examples.

Example 2-1

30	Polyvinyl alcohol	5 parts
	Distilled water	100 parts
	Non-ionic surfactant	1 part
	Finely divided silicic anhydride	5 parts
	Water-dispersible red pigment	0.5 parts

35 First, the distilled water and polyvinyl alcohol are added to a vessel equipped with a water bath or a steam heater, and heated to a temperature of 90°C while stirring.

The finely divided silicic anhydride is added during heating, and the same temperature is maintained for a period of about 2 hours. The thus obtained complete solution is then cooled to a temperature of 40°C, and the red pigment and the non-ionic surfactant are added while cooling. A water-soluble protective coating-forming composition can be obtained.

Example 2-2

10	Sodium salt of partially esterified styrene-maleic acid copolymeric resin	10 parts
	Purified water	20 parts
	Ethanol	45 parts
	Plasticizer	5 parts
15	Ethylene glycol monoethyl ether acetate	20 parts

These substances are mixed, by stirring, in a vessel equipped with a reflux condenser at a temperature of 50 through 70°C. An alkali-soluble protective coating-forming composition can be obtained.

Generally, the radiation-sensitive sheet material in accordance with the present invention, as has been already described, has the structure illustrated in Figure 1. For the purpose of producing such a radiation-sensitive sheet material, the following procedure can be used, for example. Namely, a surface of the support 10 is coated with a radiation-sensitive resin composition prepared in any one of Examples 1-1 through 1-10. Then, the coated support 10 is placed in a stream of warm air at a temperature of about 40°C to evaporate the solvent contained in the coating of the radiation-sensitive resin composition. As a result of this, a layer 11 of radiation-sensitive material is formed on the support 10. Subsequently, a protective coating-forming composition such as prepared in either Example 2-1 or 2-2 is coated on the layer 11 of the radiation-sensitive material. Thereafter, the resulting coating is completely dried in a stream of warm air at a temperature of about 40



through 50°C, whereby a radiation-sensitive sheet material having a protective coating 12 as a topcoat is obtained. For example, if it is intended to produce the radiation-sensitive sheet material which is useful in the production of cards, a transparent sheet of a rigid vinyl chloride having a thickness of 0.08 through 0.1 mm should be preferably used, and, in addition to this, the thicknesses of the layer 11 of the radiation-sensitive material and the protective coating 12 should be desirably about 4 microns and about 5 microns, respectively.

In the practical production of the radiation-sensitive sheet material, it is possible to use a web of support, and to continuously coat on the surface thereof a coating composition. The coated web is suitably cut into sheets of a standard size, packaged under light shielding conditions, and supplied to the user. The user can open a package of the sheet at the time of use.

In Figure 2, a cross-sectional view of the radiation-sensitive sheet material which has been exposed to actinic radiation through a transparent negative is illustrated. The actinic radiation passes through a transparent negative during exposure, and reaches exposed areas 11a in the layer 11 of the radiation-sensitive material of the shown sheet material. In this case, the protective coating 12 formed on the layer 11 of the radiation-sensitive material does not prevent the transmission of the actinic radiation therethrough. If the support 10 is composed of a transparent material, the actinic radiation may be irradiated from the reverse side of the support 10 through the transparent negative, as is well-known in the art. The exposed areas 11a in the layer 11 of the radiation-sensitive material become insoluble as a result of photoreaction, and adhere to the surface of the underlying support 10. The radiation-sensitive material in the unexposed areas 11b remains unreacted, and therefore its solubility inherent in the radiation-sensitive material is maintained without change. Exposure can be carried out in accordance with the

manner well-known in the art. For example, any light source capable of richly emitting ultraviolet radiation of from 2,500 to 4,200 Å, such as a three-phase arc lamp, a super-high pressure mercury vapor lamp, a chemical lamp, a metal halide lamp and the like, can be used as the exposure light source.

Figure 3 illustrates the condition of the sheet material as shown in Figure 2, after it has been immersed in a developing solution. After the sheet material is processed with the developing solution, the protective coating 12 existing thereon is completely removed, whereby only the image formed from the radiation-sensitive material in the exposed areas 11a remains. The radiation-sensitive material in the unexposed areas 11b is completely washed off as a result of development and therefore the surface of the underlying support 10 is again exposed. The remaining image coincides with the exposed areas 11a and has a counter which is clearly distinct from the surface, in the unimaged areas, of the support 10. In addition, the image has a vivid colour provided by the pigment. A processing solution used in the development is weakly alkaline. A solution suitable for the above object is, for example, a mixture consisting of 50 parts of anhydrous sodium carbonate, 5 parts of a surfactant and 10,000 parts of water.

The following examples illustrate the results obtained when the radiation-sensitive sheet material according to the present invention is used practically. However, it should be appreciated that the present invention is not limited to these examples.

#### Example 3-1

Each of the radiation-sensitive resin compositions as described in Examples 1-1 through 1-10 was separately coated on transparent, rigid vinyl chloride sheet having a thickness of 0.1 mm by means of a roll coater so that the thickness of the dried coating was 4 microns. Further, the composition as described in Example 2-1 was coated thereon to form a protective coating having a dry thickness of

5 microns. A radiation-sensitive sheet material was obtained. The resulting sheet material was placed in a vacuum printing frame, being registered with a step wedge having 21 optical photographic densities, and a negative film with transparent dotted images. The layer of the radiation-sensitive material was subjected to an exposure step by means of a 3 kw metal halide lamp, which was located 80 cm away from the radiation-sensitive sheet material, from the reverse side of the sheet material through the step wedge and the negative film, and then processed with the processing solution as described above. The processed sheet material was tested with regard to its sensitivity, developability, dot reproducibility, adhesion to vinyl chloride film, and coating strength. The results shown in the following Table II were obtained. Furthermore, when the unprocessed radiation-sensitive sheet material was tested with regard to its shelf stability, the results, also shown in the following Table II, were obtained.

Table II

Composition	Sensitivity	Develop- ability	Dot repro- ducibility	Adher- ability	Coating strength	Shelf stability
1 - 1	120 sec	⊙	○	⊙	○	less than 6 months
1 - 2	90 sec	○	○	⊙	⊙	less than 8 months
1 - 3	20 sec	⊙	⊙	⊙	⊙	more than 12 months
1 - 4	20 sec	⊙	⊙	⊙	⊙	more than 12 months
1 - 5	more than 400 sec	⊙	-	-	-	more than 12 months
1 - 6	90 sec	△	○	△	⊙	more than 12 months
1 - 7	40 sec	△	△	○	⊙	more than 12 months
1 - 8	360 sec	⊙	△	⊙	○	less than 2 months
1 - 9	180 sec	⊙	○	⊙	○	less than 2 months
1 - 10	240 sec	⊙	△	⊙	⊙	less than 6 months

As to the symbols in Table II

1. Each of the sensitivities described in the table refers to time (seconds) which was necessary to completely cure the sheet material corresponding to the first four steps of the 21 steps in the step wedge.
2. Developability:
  - ⊙ A vivid image is formed within 30 seconds, and there is no residue in unexposed areas on the support.
  - 10 ○ A vivid image is formed within 60 seconds, and there is no residue in unexposed areas on the support.
  - △ A part of the composition remains on the support, and fogging is caused in spite of development for more than 60 seconds.
  - 15
3. Dot Reproducibility:
  - ⊙ 5% of the dots of the corresponding halftone negative are correctly reproduced.
  - 10% of the dots of the corresponding halftone negative are correctly reproduced.
  - 20 △ Reproducible dots are at most 25% of the dots of the corresponding halftone negative.
4. Adherability: (According to peeling test)
  - ⊙ Adhesion of 100/100
  - 25 ○ Adhesion of 10/100
  - △ Adhesion of 0/100
5. Coating Strength:
  - ⊙ Coating is not peeled off after rubbing 50 times using a cotton ball moistened with ethanol.
  - 30 ○ Coating is slightly peeled off after rubbing 50 times using a cotton ball moistened with ethanol.
  - △ Coating is completely peeled off after rubbing 50 times using a cotton ball moistened with ethanol.
  - 35
6. Shelf Stability:

Storageable duration at room temperature.

Example 3 - 2

The procedure similar to that as described in  
Example 3 - 1 was repeated except that the composition as  
5 described in Example 2 - 2 was used in place of the com-  
position of Example 2 - 1 used in Example 3 - 1. Results  
similar to those described in the above Table II were  
obtained.

CLAIMS

1. A photopolymerizable radiation-sensitive resin composition comprising a styrene-maleic acid copolymeric resin as well as an ethylenically unsaturated compound and a photopolymerization initiator.
- 5        2. A composition as defined in Claim 1 wherein said styrene-maleic acid copolymeric resin has a molecular weight of 1,000 through 2,000 and an acid value of 130 through 220.
- 10       3. A composition as defined in Claim 2 wherein said styrene-maleic acid copolymeric resin is a partially esterified styrene-maleic anhydride resin which contains remaining carboxyl groups in its molecule.
- 15       4. A composition as defined in claim 1 wherein said ethylenically unsaturated compound has one or more ethylene groups.
- 20       5. A composition as defined in Claim 4 wherein said ethylenically unsaturated compound has a molecular weight of 150 or more and a boiling point, under normal pressure, of 100°C or more.
- 25       6. A composition as defined in Claim 1 wherein said ethylenically unsaturated compound is a mixture of one or more ethylenic compounds with at least one acryloyl or methacryloyl group and a terminal hydroxyl group selected from the group consisting of polyester monoacrylate, 2-hydroxyethyl acrylate and 1,4-butylene glycol mono-  
30       acrylate, and one or more ethylenic compounds with at least one acryloyl or methacryloyl group selected from the group consisting of polyethylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butylene glycol diacrylate, 1,6-hexane glycol diacrylate, neopentyl glycol diacrylate, 2,2-bis(4-acryloxy diethoxy phenyl)propane, 2,2-bis(4-acryloxy propyloxy phenyl)propane, trimethylol propane tri-  
35       acrylate, tetramethylol methane triacrylate, ethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, 1,6-hexane glycol dimethacrylate, polypropylene glycol dimethacrylate, 2,2-bis(4-methacryloxy ethoxy phenyl)propane,

2,2-bis(4-methacryloxy diethoxy phenyl)propane, trimethylol propane trimethacrylate, polyester acrylate oligomer, polyamide acrylate, epoxy acrylate, polyurethane acrylate and polyester monoacrylate.

5        7. A composition as defined in Claim 1 wherein said photopolymerization initiator is one or more compounds selected from the group consisting of acyloin, acyloin derivatives, ketones, substituted benzophenones, aldehydes and substituted or unsubstituted polynuclear quinones.

10       8. A composition as defined in Claim 1, which further comprises a pigment.

9. A composition as defined in Claim 1, which comprises said styrene-maleic acid copolymeric resin as well as 10 through 60% by weight, based on the weight of  
15 said copolymeric resin, of said ethylenically unsaturated compound and 1 through 10% by weight, based on the total weight of said copolymeric resin and said ethylenically unsaturated compound, of said photopolymerization initiator.

10. A composition as defined in Claim 9 wherein a  
20 ratio, of percentage by weight, of said ethylenic compound with at least one acryloyl or methacryloyl group having a terminal hydroxyl group to that having no terminal hydroxyl group is 40 through 60%.

11. A composition as defined in Claim 9, which  
25 further comprises 1 through 50 parts by weight, based on 100 parts by weight of the composition, of said pigment.

12. A radiation-sensitive sheet material comprising a support and, at least, a layer of a radiation-sensitive material coated on one side of the support, said layer of  
30 the radiation-sensitive material being a layer of a photopolymerizable radiation-sensitive resin composition which comprises a styrene-maleic acid copolymeric resin as well as an ethylenically unsaturated compound and a photopolymerization initiator.

13. A sheet material as defined in Claim 12 wherein  
35 said photopolymerizable radiation-sensitive resin composition further comprises a pigment.



14. A sheet material as defined in Claim 12 wherein a protective coating is further coated over said layer of the radiation-sensitive material.

5 15. A sheet material as defined in Claim 14 wherein said protective coating comprises a water-soluble resin.

16. A sheet material as defined in Claim 15 wherein said water-soluble resin comprises polyvinyl alcohol.

10 17. A sheet material as defined in Claim 16 wherein said polyvinyl alcohol is a partially saponified product of polyvinyl alcohol and has a degree of polymerization of 1,000 through 1,500 and a degree of saponification of 80% or less.

15 18. A sheet material as defined in Claim 15 wherein said protective coating further comprises a nonionic surfactant or saponin.

19. A sheet material as defined in Claim 14 wherein said protective coating comprises an alkali-soluble resin.

20 20. A sheet material as defined in Claim 19 wherein said alkali-soluble resin is selected from the group consisting of a styrene-maleic acid copolymeric resin, a partially esterified styrene-maleic acid copolymeric resin and an alkali salt of the styrene-maleic acid copolymeric resin.

## C L A I M S

1. (Amended) A photopolymerizable radiation-sensitive resin composition comprising a styrene-maleic acid copolymeric resin, and,

a combination of an ethylenically unsaturated compound which is a mixture of the following compounds (A) and (B):

(A) one or more ethylenic compounds having a molecular weight of 150 or more, a boiling point, under normal pressure, of 100°C or more, at least one acryloyl or methacryloyl group, and a terminal hydroxyl group, and;

(B) one or more ethylenic compounds having a molecular weight of 150 or more, a boiling point, under normal pressure, of 100°C or more, and at least one acryloyl or methacryloyl group;

and a photopolymerization initiator which comprises benzyl and dimethyl amino benzaldehyde.

2. A composition as defined in Claim 1 wherein said styrene-maleic acid copolymeric resin has a molecular weight of 1,000 through 2,000 and an acid value of 130 through 220.

3. A composition as defined in Claim 2 wherein said styrene-maleic acid copolymeric resin is a partially esterified styrene-maleic anhydride resin which contains the remaining carboxyl group in its molecule.

4. (Deleted)

5. (Deleted)

6. A composition as defined in Claim 1 wherein said ethylenically unsaturated compound is a mixture of one or more ethylenic compounds with at least one acryloyl or methacryloyl group and a terminal hydroxyl group selected from the group consisting of polyester monoacrylate, 2-hydroxyethyl acrylate and 1,4-butylene glycol monoacrylate, and one or more ethylenic compounds with at least one acryloyl or methacryloyl group selected from the group consisting of polyethylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butylene glycol diacrylate, 1,6-hexane glycol diacrylate, neopentyl glycol diacrylate, 2,2-bis(4-acryloxy diethoxy phenyl) propane, 2,2-bis(4-acryloxy propyloxy phenyl) propane, trimethylol propane triacrylate, tetramethylol methane triacrylate, ethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, 1,6-hexane glycol dimethacrylate, polypropylene glycol dimethacrylate, 2,2-bis(4-methacryloxy ethoxy phenyl) propane, 2,2-bis(4-methacryloxy diethoxy phenyl) propane, trimethylol propane trimethacrylate, polyester acrylate oligomer, polyamide acrylate, epoxy acrylate, polyurethane acrylate and polyester monoacrylate.

7. (Deleted)

8. A composition as defined in Claim 1, which further comprises a pigment.

9. A composition as defined in Claim 1, which comprises said styrene-maleic acid copolymeric resin as well as 10 through 60% by weight, based on the weight of said copolymeric resin, of said ethylenically unsaturated compound and 1 through 10% by weight, based on the total weight of said copolymeric resin and said ethylenically unsaturated compound, of said photopolymerization initiator.

10. A composition as defined in Claim 9 wherein a ratio, of percentage by weight, of said ethylenic compound

with at least one acryloyl or methacryloyl group having a terminal hydroxyl group to that having no terminal hydroxyl group is 40 through 60%.

11. A composition as defined in Claim 9, which further comprises 1 through 50 parts by weight, based on 100 parts by weight of the composition, of said pigment.

12. (Amended) A radiation-sensitive sheet material comprising a support and a layer of a radiation-sensitive material coated on at least one side of the support, said layer of the radiation-sensitive material being a layer of a photopolymerizable radiation-sensitive resin composition which comprises a styrene-maleic acid copolymeric resin, and,

a combination of an ethylenically unsaturated compound which is a mixture of the following compounds (A) and (B):

(A) one or more ethylenic compounds having a molecular weight of 150 or more, a boiling point, under normal pressure, of 100°C or more, at least one acryloyl or methacryloyl group, and a terminal hydroxyl group, and;

(B) one or more ethylenic compounds having a molecular weight of 150 or more, a boiling point, under normal pressure, of 100°C or more, and at least one acryloyl or methacryloyl group;

and a photopolymerization initiator which comprises benzyl and dimethyl amino benzaldehyde.

13. A sheet material as defined in Claim 12 wherein said photopolymerizable radiation-sensitive resin composition further comprises a pigment.

14. A sheet material as defined in Claim 12 wherein a protective coating is further coated over said layer of the radiation-sensitive material.

15. A sheet material as defined in Claim 14 wherein said protective coating comprises a water-soluble resin.

16. A sheet material as defined in Claim 15 wherein said water-soluble resin comprises polyvinyl alcohol.

17. A sheet material as defined in Claim 16 wherein said polyvinyl alcohol is a partially saponified product of polyvinyl alcohol and has a degree of polymerization of 1,000 through 1,500 and a degree of saponification of 80% or less.

18. (Deleted)

19. A sheet material as defined in Claim 14 wherein said protective coating comprises an alkali-soluble resin.

20. (Deleted)

STATEMENT BASED ON THE PROVISIONS OF ARTICLE 19 (1),  
OF PATENT COOPERATION TREATY

The claims described in the replacement sheets differ from those originally filed, with regard to the following points.

- (1) Claim 1 was amended to specify an ethylenically unsaturated compound and a photopolymerization initiator used in a photopolymerizable radiation-sensitive resin composition according to the invention of this application.
- (2) Claim 4 was deleted as a result of the amendment of Claim 1.
- (3) Claim 5 was deleted as a result of the amendment of Claim 1.
- (4) Claim 7 was deleted as a result of the amendment of Claim 1.
- (5) Claim 12 was amended to specify an ethylenically unsaturated compound and a photopolymerization initiator used in a radiation-sensitive sheet material according to the invention of this application.
- (6) Claim 18 was deleted.
- (7) Claim 20 was deleted.

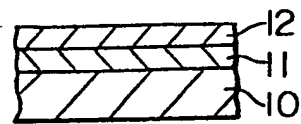
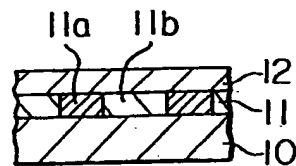
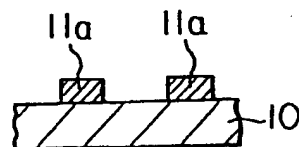
*Fig. 1**Fig. 2**Fig. 3*

TABLE OF REFERENCE NUMERALS  
AND PARTS

Reference Numerals	... Parts
10	... Support
11	... Layer of radiation- -sensitive material
11a	... Exposed areas
11b	... Unexposed areas
12	... Protective coating



## INTERNATIONAL SEARCH REPORT

International Application No. **0035574** PCT/JP80/00198

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>2</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl. <sup>3</sup> G03C1/68, C08F2/48, C08L35/06, G09F7/00		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>4</sup>		
Classification System	Classification Symbols	
I P C	G03C1/68, C08F2/48, C08L35/06, G09F7/00	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>4</sup>		
Jitsuyo Shinan Koho 1960 - 1980		
Kokai Jitsuyo Shinan Koho 1971 - 1980		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>16</sup>		
Category <sup>*</sup>	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
X	JP, A 49-114416 1974-10-31 Matsumoto Shigeji and one other	1-20
X	JP, A 49-114417 1974-10-31 Matsumoto Shigeji and one other	1-20
X	JP, A 47-6330 1972-4-8 Kalle AG.	1-20
X	Jaromir Kosar "Light-Sensitive Systems" 1965 John Wiley & Sons. Inc. U.S.p.160-167	1-20
X	Nagamatsu Gentaro and one other "Kankosei Kobunshi" Kodansha Kabushiki Kaisha P. 233-239	1-20
<p><sup>*</sup> Special categories of cited documents: <sup>18</sup></p> <p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but on or after the priority date claimed</p> <p>"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search <sup>2</sup>		Date of Mailing of this International Search Report <sup>2</sup>
November 18, 1980 (18.11.80)		December 1, 1980 (01.12.80)
International Searching Authority <sup>1</sup>		Signature of Authorized Officer <sup>20</sup>
Japanese Patent Office		

TC1700

REMCEN

Organization

U.S. DEPARTMENT OF  
COMMISSION

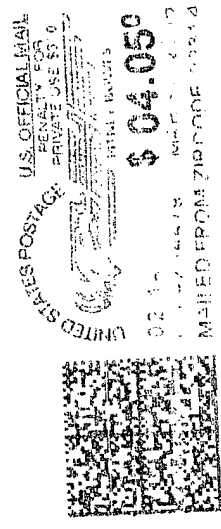
PO BOX 1450

ALEXANDRIA, VA 22313-1450

IF UNDELIVERABLE RETURN IN TEN DAYS

OFFICIAL BUSINESS

AN EQUAL OPPORTUNITY EMPLOYER



**RTS**  
RETURN TO SENDER

☐ A ☐ INSUFFICIENT ADDRESS  
☐ C ☐ ATTEMPTED NOT KNOWN  
☐ S ☐ SUCH NUMBER/STREET  
NOT DELIVERABLE AS ADDRESSED  
- UNABLE TO FORWARD

☐ OTHER

RECEIVED  
APR 07 2006  
USPTO MAIL CENTER

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**